Reprinted from

Neblette's Handbook of Photography and Reprography

Materials, Processes and Systems

Seventh Edition

Edited by
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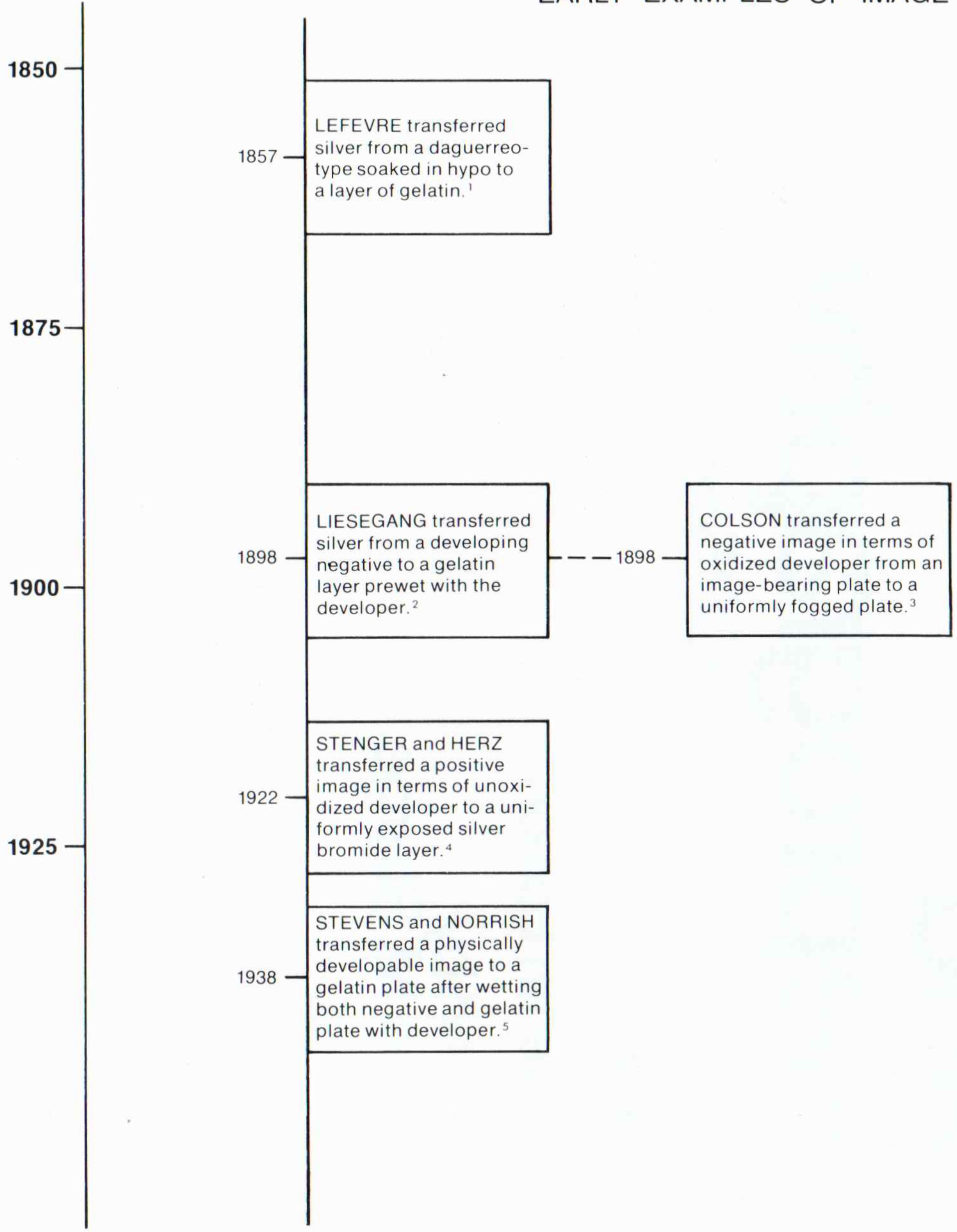
VAN NOSTRAND REINHOLD COMPANY
NEW YORK CINCINNATI ATLANTA DALLAS SAN FRANCISCO
LONDON TORONTO MELBOURNE

EARLY EXAMPLES OF IMAGE TRANSFER PHENOMENA



LEFEVRE transferred silver from a daguerreotype soaked in hypo to a layer of gelatin.[1]

LIESEGANG transferred silver from a developing negative to a gelatin layer prewet with the developer.[2]

COLSON transferred a negative image in terms of oxidized developer from an image-bearing plate to a uniformly fogged plate.[3]

STENGER and HERZ transferred a positive image in terms of unoxidized developer to a uniformly exposed silver bromide layer.[4]

STEVENS and NORRISH transferred a physically developable image to a gelatin plate after wetting both negative and gelatin plate with developer.[5]

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CLASSIFICATION AND CHRONOLOGY OF PRINCIPAL IMAGE TRANSFER SYSTEMS

PROCESSING MATERIALS	**Multiple Solutions and Washes**		**Single Solution**		**Pod/Viscous Reagent**	
PROCESSING EQUIPMENT	Tanks or Trays		Tank/Rollers	Web Transport/Rollers	Camera with Rollers	
FILM PROPERTIES	Low Speed Materials for Use in Reprography			High Speed Materials for Camera Originals		
	Continuous Tone	High Contrast (Line Copy)		Continuous Tone		High Contrast
1940		**TRANSARGO** (Gevaert)[6] **VERIFLEX** (Agfa)[6]				
1947	**DIAVERSAL** (Gevaert)[6 7]				LAND demonstrated one-step camera and film, sepia print process.[11 12]	
1948					**TYPE 40**, speed 100 (Polaroid)[12]	
1949			**COPYRAPID** (Agfa)[6 7]			
1950			**GEVACOPY** (Gevaert)[6 7]		**TYPE 41** Black and White, speed 100 (Polaroid)[12]	
1955					**TYPES 42, 43, 44**, speeds 200, 400 (Polaroid)[12]	
1957					**TYPE 46** Transparency, speed 800 (Polaroid)[12]	
1958			**CT**: Chemical Transfer (Kodak)[7] **GEVACOPY** Aluminum Offset (Gevaert)[6 7 10]			
1959					**TYPE 47**, speed 3000 (Polaroid)[12]	
1960			**CT** Offset Aluminum Plates and Paper (Kodak)[13]			
1961					**TYPE 55 P/N** Positive/ Negative (Polaroid)[12]	**TYPE 146L** Polaline (Polaroid)[12] **TYPE 410** Polascope, speed 10,000 (Polaroid)[12]
1963				TARKINGTON demonstrated continuous web processing of negative and positive: **BIMAT** (Kodak)[6 7 8 9]	LAND et al. demonstrated one-step color print process: **POLACOLOR** (Polaroid)[12 14]	
1965				**DITRECON** (Singer)[6 7]		
1967			**COPYRAPID DRY** (Agfa)[6 7] **INSTAFAX** (Kodak)[7]			
1969			**PMT**: Photomechanical Transfer (Kodak)[7]			
1972					LAND demonstrated fully integral color film, metallized dye developers: **SX-70** (Polaroid)[12 15 16]	
1975					**POLACOLOR 2** (Polaroid)[12]	
1976					**PR10** (Kodak)[17]	

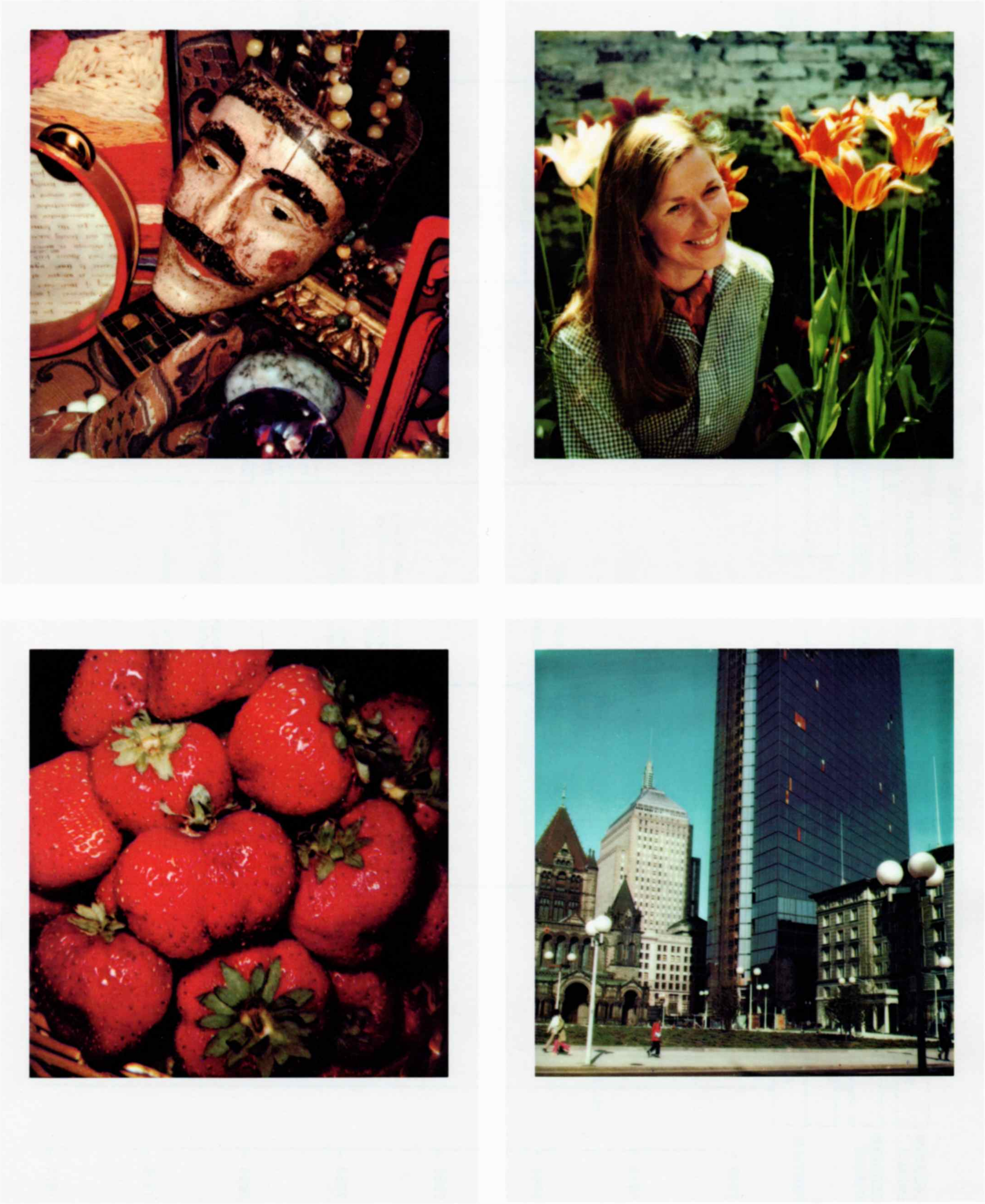

Fig. 12-1. Reproductions of the first published SX-70 prints, used as illustrations in Ref. 3a.

12

ONE-STEP PHOTOGRAPHY*

Edwin H. Land,
Howard G. Rogers
and Vivian K. Walworth

INTRODUCTION

Polaroid one-step photography combines into a nearly simultaneous set of operations the taking of a photograph, the processing of negative and positive images and the viewing of the finished print or transparency. Processing in a single step is accomplished by incorporating a photosensitive emulsion, an image-receiving system and a minute amount of totally enclosed viscous processing reagent into a film assembly and including in the camera or film carrier a mechanism for releasing and applying the reagent. Once applied, the reagent concomitantly develops the negative and deposits the positive image, each in the appropriate layer or layers of a multilayer system. Although this outwardly dry processing operation involves an intricate family of carefully controlled physical, chemical and mechanical events, they proceed automatically and the user need not be aware of their complexity.

The one-step systems readily yield pictures having excellent image quality. The film speeds are high, so that the camera may usually be hand-held. With most of the one-step cameras exposure is controlled automatically. The photographer can make pictures quickly and easily; given the opportunity to view immediately picture and subject together, he can fully evaluate his work and proceed creatively on the basis of his own evaluation.

With one-step pack and roll film cameras the photographer, after making an exposure, initiates processing by pulling a paper tab or leader. Inside the camera this action draws negative and positive sheets together through a pair of pressure rollers, releasing and spreading reagent between the two sheets. After a short, specified interval the photographer peels the sheets apart and views the photograph.

The newest Polaroid one-step system, SX-70, completely automates the procedure. To make an SX-70 picture the photographer simply presses the shutter release button. Exposure and processing follow in sequence, with the film unit ejected from the camera between motorized pressure rollers which release and spread the reagent. Image formation proceeds to completion within the ejected film unit. There is no timing or peeling apart; the photographer may watch the emerging image or may immediately take another picture.

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*In the previous edition one-step photography was discussed together with document copy photography in a chapter entitled "Diffusion-Transfer Reversal Materials" because processes in both fields involved reversal by transfer of soluble silver images. From the start, however, the two fields have differed significantly in characteristics ranging all the way from initial emulsion requirements and processing mode to final image properties; continuing growth and development in both fields has served to increase the distinction. Color processes, which now predominate in one-step photography, have no parallel in document copying, and the respective black and white processes have little in common.

In this edition the two fields are accordingly discussed in separate chapters. The earlier title is not used, as it does not adequately define the subject matter of either chapter. The preceding chapter, "Reprographic and Web Image Transfer Processes," covered contributions in the copying field, principally by Agfa-Gevaert, and in rapid, continuous image transfer systems, such as those of Kodak and Singer. This chapter will describe Polaroid's contributions in one-step photography. The chart on pp. 256–7 outlines in chronological and schematic form early observations of image transfer phenomena and the development of major products and processes covered in both chapters.

Land first described and demonstrated one-step photography in February, 1947, before the Optical Society of America.[1] He outlined the theoretical considerations involved in designing one-step systems, broadly describing the entire field in addition to the process shown. The discussion delineated the practical requirements and the resulting plan which had been chosen to provide the desired simplicity of taking and viewing pictures.

In introducing one-step photography to the Royal Photographic Society in 1949,[2] Land stressed the opportunity afforded the creative photographer by the new medium and described the primary specifications for camera and process:

> By making it possible for the photographer to observe his work and his subject simultaneously, and by removing most of the manipulative barriers between the photographer and the photograph, it is hoped that many of the satisfactions of working in the early arts can be brought to a new group of photographers .... From this photographic purpose there follows a chain of consequences, aesthetic, mechanical, and chemical, that direct and restrict the design of the camera and the character of the process. The picture must be available promptly after it is taken, and must be large enough for evaluation .... The camera should be as small and as light as is consistent with the picture size chosen, and should be dry and easy to load. The process must be reliable, safe, dry or apparently dry ....The process must be concealed from—nonexistent for—the photographer, who by definition need think of the art in *taking* and not in *making* photographs .... In short, all that should be necessary to get a good picture is to *take* a good picture, and our task is to make that possible.
>
> With this aggregation of desiderata in mind, the camera and process were contemplated as interwoven fields of investigation .... the decision that the camera must be really dry—having neither fountain pen sacs, nor damp sponges, nor sprays, nor wet rolls—took some courage, because it implied that what the camera was to do to the film must be done with extraordinary simplicity, and that what the film was to do itself was to be unusual. Thus, the camera in our initial consideration was permitted to contain, beyond the ordinary possessions of any camera, a pair of small-diameter pressure rollers, and a flat, dry, dark chamber into which the film passed after traversing the gap between these rollers. The pressure during this traversal was to convert the exposed negative into the finished, positive, stable, dry picture.

CURRENT ONE-STEP PHOTOGRAPHY*

The SX-70 System

In May, 1972, Land reported to the Society of Photographic Scientists and Engineers on a new camera, new film and new process.[3a] Together these comprise the SX-70 system, described as "Absolute One-Step Photography" because it reached for the first time and indeed transcended the earliest objectives. The new system was a marked advance in one-step photography using in combination innovative camera design and greatly advanced technology in optics, electronics and chemistry.[3a,b]

With the SX-70 camera the photographer, after composing and focusing through the single lens reflex viewer,[3a,4a,b] touches an electric trigger. Within four-tenths of a second after the shutter closes, the film unit emerges from the front of the camera. The film unit is hard, dry, shiny, flat—and the image is invisible. Initially, the image area—within a white border—is a uniform pale green. Over the next minute or two a visible image materializes with enough color and definition for judgment of its merit. The materialization continues over a few minutes to provide the final full-color picture. Since the picture emerges from the camera directly into the light, with nothing to be peeled away, the photographer has the opportunity to observe the whole process of materialization. The photographer is not concerned with wet processing of negatives or timing of prints; therefore, he is free to take his next picture as soon as he wishes. Indeed, he may take another within 1.5 sec.

The images have no visible grain; the outer surface is also free from structure, and the density range in the image is high. The result is an interesting sense of tone continuity and a feeling of space in the shadows. Figure 12-1 reproduces pictures made by the SX-70 process, and Fig. 12-2 demonstrates the materialization of an image from the initial, invisible state to its final full color.

The SX-70 Film. The picture unit which is expelled from the camera is rectangular with three narrow borders and one wide border around a picture, ca. 8 by 8 cm. The film pack contains 10 of these units, a dark slide which is the same size as the unit, and a fresh battery[5] which is also the size and shape of the film unit. Since there are no accessory papers, leaders or connectors between picture units, the total pack is relatively thin. Furthermore, the picture units fit snugly in the pack, allowing it to be compact in all dimensions.

Structure and Components of Picture Unit. At the time of exposure each picture unit[6] consists of an integral

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*This section discusses the present-day scope of Polaroid one-step photography, with particular emphasis on the SX-70 system and its components. The following section covers concepts basic to the design of one-step cameras and image processes, along with an account of Land's early experiments in image transfer and a summary of the resulting specifications for a practical one-step process. The last two sections trace the parallel evolution of the Polaroid silver image processes and dye image processes, respectively, and describe research relating to their design and performance.

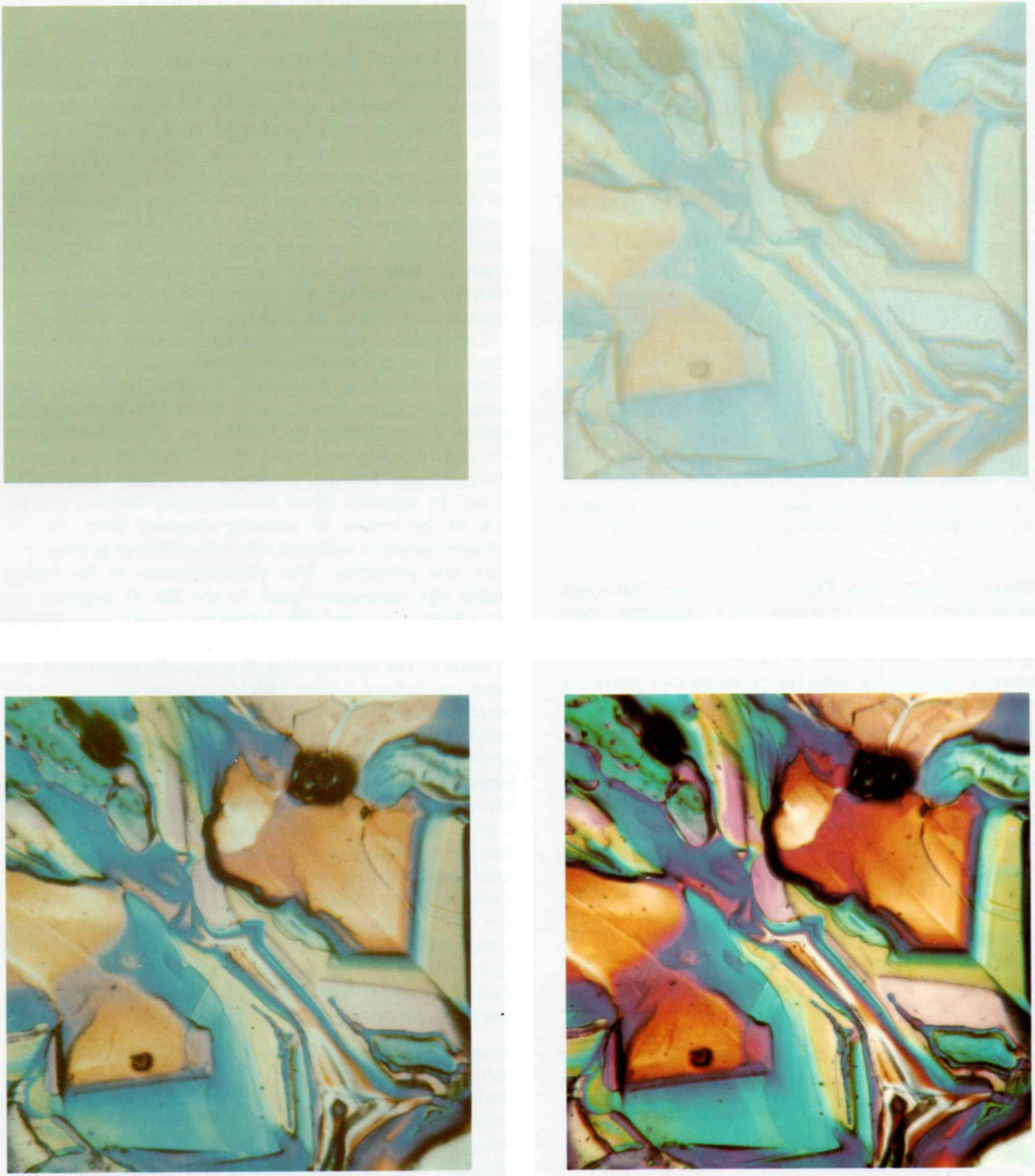
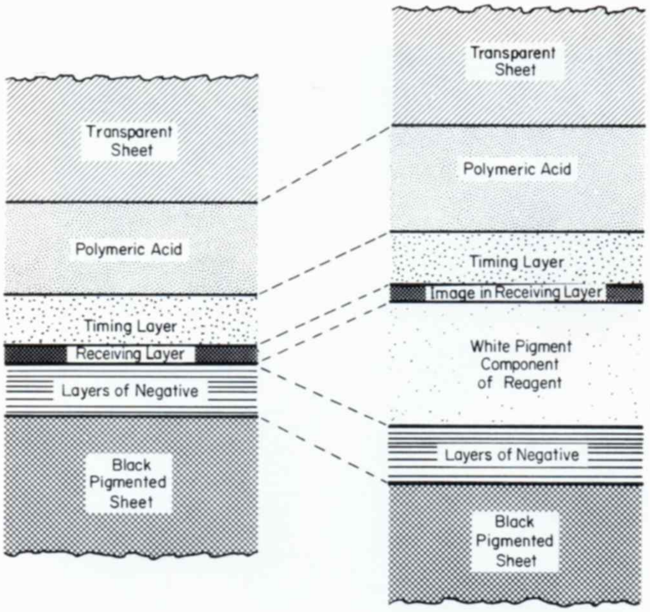


Fig. 12-2. Stages in the materialization of an SX-70 image. The color print becomes visible as the opacifying dyes become colorless. The subject is crystalline silver nitrate between crossed polarizers, photographed at 80X.



(a) Before spreading reagent (b) After image formation

Fig. 12-3. Schematic cross sections of SX-70 film unit (a) before and (b) after development, drawn approximately to scale.

multilayer structure. (See Fig. 12-3). The outer two layers comprise most of the thickness, their thickness being selected as the minimum necessary to give a good feeling of rigidity and flatness. One of these two outer sheets is transparent, so that the light for exposure can penetrate through it into the integral structure, and the other one is opaque black. Both the clear and black-pigmented sheets are polyester, and the resulting structural symmetry ensures that the pictures stay flat under all conditions.*

The wide border of the picture unit conceals a very thin version of the Polaroid pod.** The borders are made of materials that are tough and accurately dimensioned. This material serves the aesthetic function of providing white margins, holds the integral structure intact, and helps to determine the distance apart of two inner layers of the integral structure when the viscous reagent within the pod is redistributed throughout the whole area in the processing mode. To achieve well-controlled processing under the special conditions defined by the compact film design, both the pod and the reagent spreading system had to undergo what Land called a forced evolution. He described the exigencies this way:

> We had to learn precision in filling the pods far beyond what we had previously regarded as precision. We had to learn to make a thin spread between layers already in place. We had to learn to make a square spread. We had to learn to keep the residue at the end of the spread miniscule, and we had to learn to conceal this miniscule residue.[3a]

The integral picture unit contains no air spaces,[8] either before or after processing, as shown in the schematic drawings of Fig. 12-3. The whole inner structure within the two heavy layers has a total thickness of less than 2 mils (50 μm). Of this, the layers which constitute the negative are less than a third. The compactness of the SX-70 picture unit at each stage emphasizes the precision required. Nothing is added and nothing is discarded. Each component is present in the appropriate amount, and the total structure so composed is internally compatible and stable both as an unprocessed picture unit and as the finished full color picture.

The positive image-forming components of the SX-70 film unit are dye developers,[9] molecules which combine the light-absorbing properties of subtractive image dyes with the reactive functions of silver halide developing agents. Solubilization and diffusion of a dye developer are controlled by reactions of the developer portion of the molecule. The dye developer is initially insoluble in water. In aqueous alkali the developer forms a soluble salt; in the course of reducing exposed silver the developer moiety is oxidized, and its oxidation product has very low solubility. The chromophores of the highly stable dye developers used in the SX-70 negative are metallized dyes, and the developer moiety now used is hydroquinone.***

Each of the dye developers is initially positioned in a layer just behind a silver halide emulsion by which it will be controlled during processing. In each case the spectral sensitivity of the emulsion is complementary to the absorption of the dye developer it overlies. The color negative thus comprises three monochrome units—a blue-sensitive emulsion overlying a yellow dye developer, a green-sensitive emulsion over a magenta dye developer and a red-sensitive emulsion over a cyan dye developer. In addition there are spacer layers to control interactions between the three monochrome units. Figure 12-4 shows the spectral response of an SX-70 picture film unit in terms of the three transferred dye developers. The spectral response of each emulsion is a consequence of both its spectral sensitivity and optical filtration by the overlying structure.

Image Formation. When the SX-70 film unit passes through the rollers immediately after exposure, the pod sealed within the unit ruptures and the small quantity of viscous reagent forces its way between two layers of the integral structure, forming immediately a new integral structure with an inner stratum of white pigment, water, opacifying dyes,[10] an alkali, such as potassium hydroxide, and other photographically active materials. The potassium hydroxide penetrates the layers of the negative in about a second. It dissolves the dye developers by ionizing the developer groups and similarly solubilizes a small, mobile auxiliary developer molecule, such as

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*The improved SX-70 film introduced in 1976 includes a durable optical quarter-wave anti-reflection coating on the outer surface of the clear polyester sheet.[7] The reduced reflectivity minimizes flare and increases the efficiency of transmission both in exposure of the negative and in viewing of the final image.

**Pod structures and functions are discussed in detail on page 282.

***Dye developers are discussed further in the section on Dye Image Processes, p. 318.

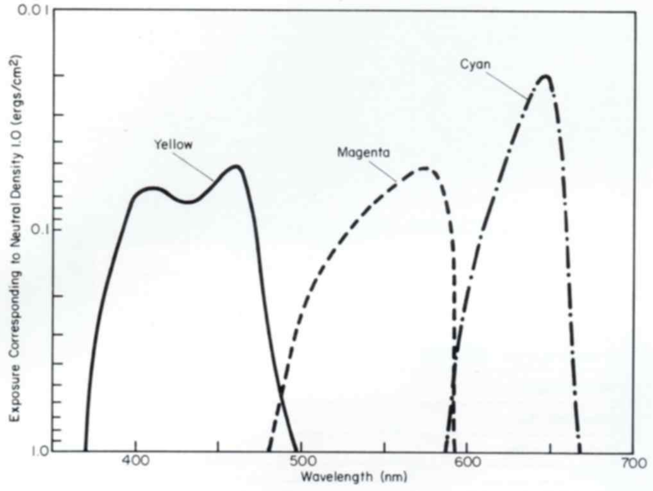

Fig. 12-4. Spectral response of an SX-70 film unit, displayed in terms of transferred dye developer. Each curve shows the spectral distribution of exposures corresponding to transfer of an amount of dye developer equivalent to that contained in a neutral gray area of density 1.0. The curve shape for each dye developer is a consequence of both the spectral sensitivity of the emulsion which controls that dye and optical filtration by the overlying layers of the integral structure.

methyl phenyl hydroquinone (MPHQ), which may be included either in the structure of the negative or in the reagent (Eqs. (a) and (b), Fig. 12-5). The auxiliary developer is similar in structure to the dye developers but, since it does not have a large dye moiety, this developer can move rapidly through all of the layers of the negative.

As soon as the alkali reaches and solubilizes the dye developers they are capable of moving from their original layers throughout the structure. In each emulsion layer, where the silver halide has been fully exposed, the auxiliary developer, which may be regarded as a "messenger," transfers an electron to a silver ion of the exposed silver halide, reducing the silver halide to silver and generating a semiquinone ion radical. The semiquinone radical, which lacks one electron, in turn takes an electron from a dye developer molecule, thus returning to its original state and leaving the dye developer in the semiquinone state. (Eqs. (c) and (d), Fig. 12-5). The process may be aided by a quaternary salt, originally present in the reagent, which "insolubilizes" the oxidized dye developer. Although the reaction between oxidized dye developer and quaternary yields a precipitate *in vitro*, it is sufficient if in the developing areas the dye developer, in association with the quaternary, forms a much less mobile molecule.*

In unexposed regions the solubilized dye developer passes through the overlying emulsion and on through the other layers into the image-receiving layer, where it is captured by a polymeric mordant.

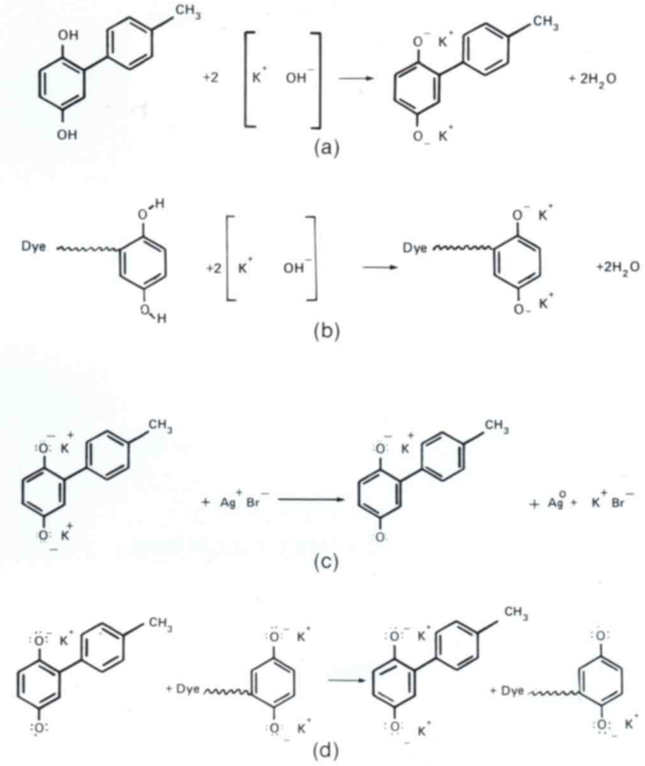

Fig. 12-5. Chemical steps of the SX-70 process include (a) formation of a soluble salt of the auxiliary developer, (b) formation of a soluble salt of the dye developer, (c) reduction of exposed silver halide by the auxiliary developer, and (d) oxidation of dye developer by the semiquinone ion radical of the auxiliary developer.

Potassium hydroxide, of great importance to all of the processes being discussed, diffuses from the reagent toward all the layers of the film unit. It permeates the layers of the negative in a second, whereas its migration to the polymeric acid layer on the positive support sheet is inhibited initially by a timing layer. The polymeric acid is present as a mechanism for decreasing the alkalinity of the developing picture, as well as for providing a sink from which the potassium ions cannot escape. When potassium ions reach the polymeric acid they are captured, forming an immobile salt of the high polymer.

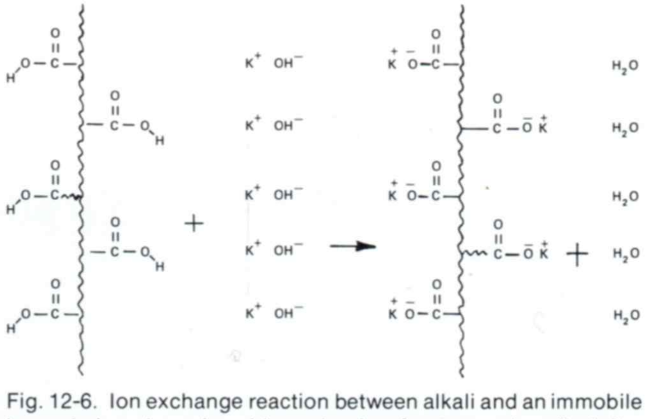

Fig. 12-6. Ion exchange reaction between alkali and an immobile long-chain polymeric acid, mechanism for decreasing alkalinity.

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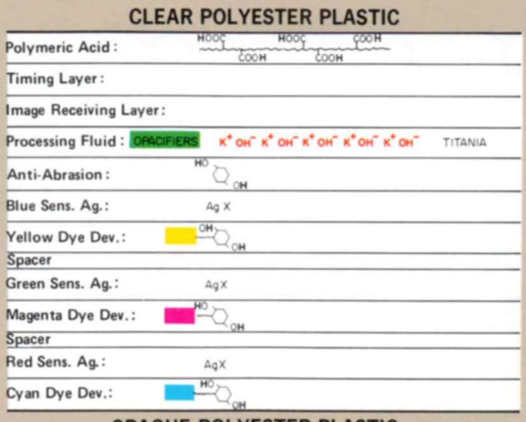
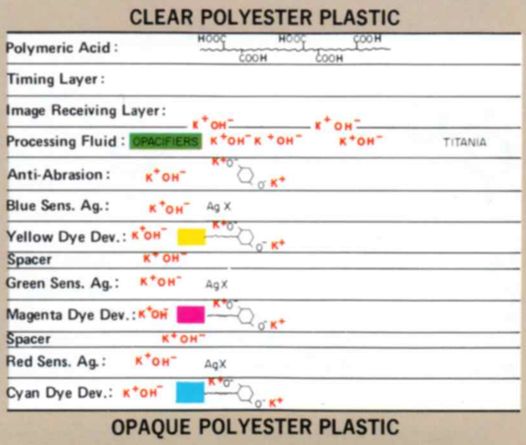
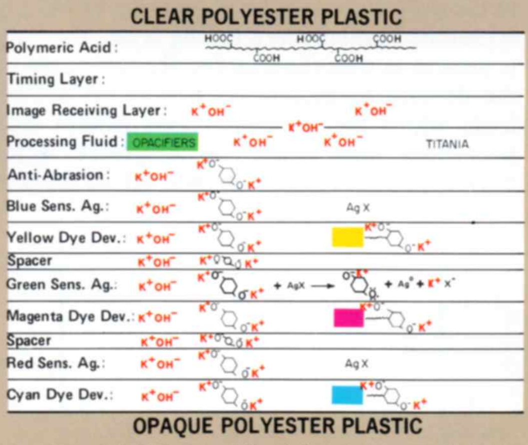
*Though quaternaries are very useful, they are not necessary. Figure 12-80d (page 320) reproduces a print from a preproduction Polacolor film (1957), an example of a system in which dye developers are well controlled without the use of quaternaries. Interlayers of the negative comprising cellulose acetate hydrogen phthalate and cellulose acetate provided a hold-release mechanism.



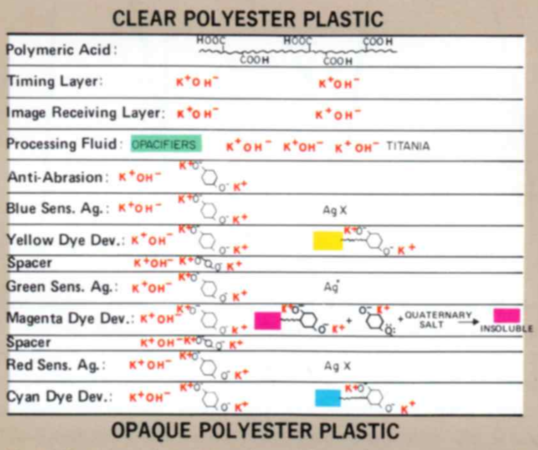
A. A stratum is inserted. This portion of the film has been exposed to green light.



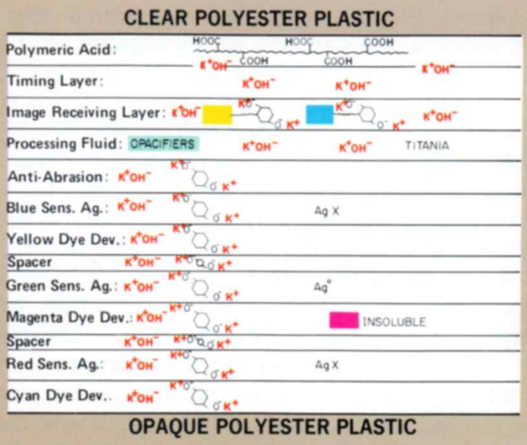
B. The potassium ions permeate the negative, ionizing the dye developers and the MPHQ.



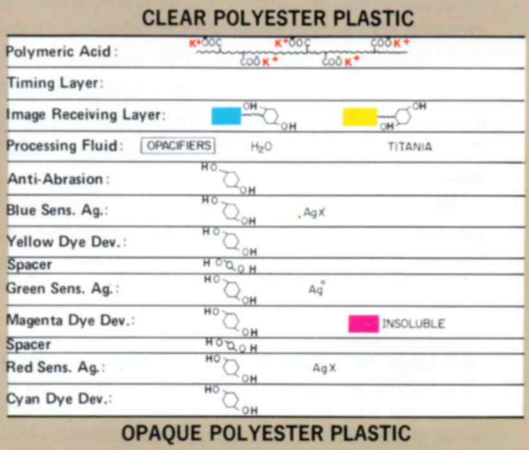
C. The MPHQ is oxidized by the exposed silver halide.



D. The dye developer is oxidized by the oxidized MPHQ and the latter is reduced.



E. The cyan and yellow dye developers, unoxidized, transfer; the magenta dye-developer, oxidized, is immobilized in or near the green sensitive emulsion.



F. The Sea of Tranquility: the potassium ions now reach the polymeric acid and are captured. All significant components throughout the whole 17 layer structure are immobilized.

Fig. 12-7. Conceptual diagram of the sequential steps involved in formation of an SX-70 image.

The long chain polymer acts as an ion exchanger. As the potassium ions form the salt of the polymer, freed hydrogen ions react with the hydroxyl ions to form water (See Fig. 12-6.) The water is a useful reaction product, for it diffuses and helps to keep the process going.

The reduction of alkali concentration accomplishes two important functions simultaneously: the transferred image is stabilized as the image-forming dyes become less mobile, and the opacifying dyes are decolorized. Figure 12-7 presents in diagram form the sequence of reactions which take place from the time that alkali ions, initially present in only the reagent layer, begin to permeate the negative until they are finally captured in the polymeric acid layer.

The three transferred dye developer images together form the final positive image which is seen against the background of the white titania pigment. Figure 12-8 shows the individual spectra of three dye developer images which together form a neutral image of density 1.0. Figure 12-9 illustrates the formation of color images schematically, and Fig. 12-10 shows actual cross sections of an SX-70 negative before and after processing.

Opacification. In order that the developing film may exit from the camera while still sensitive and not be fogged by ambient light, which may be several hundred

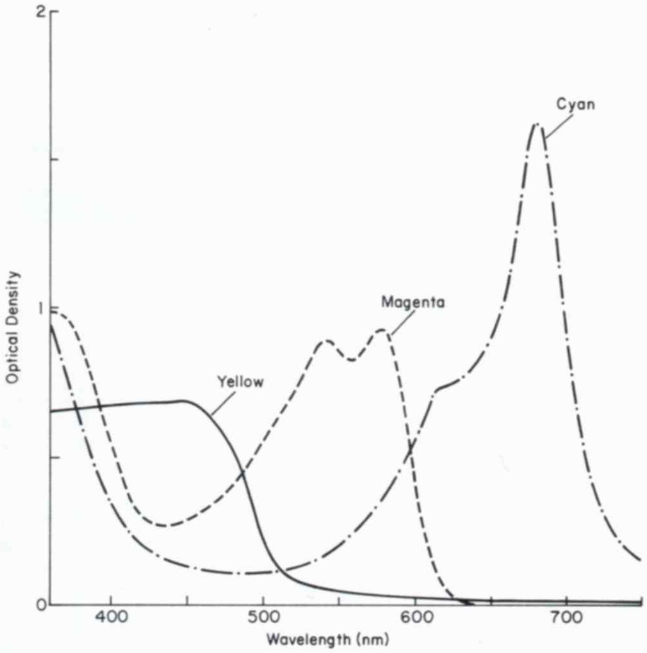


Fig. 12-8. Absorption spectra of cyan, magenta and yellow dye developer images which together form a visually neutral image of density 1.0.

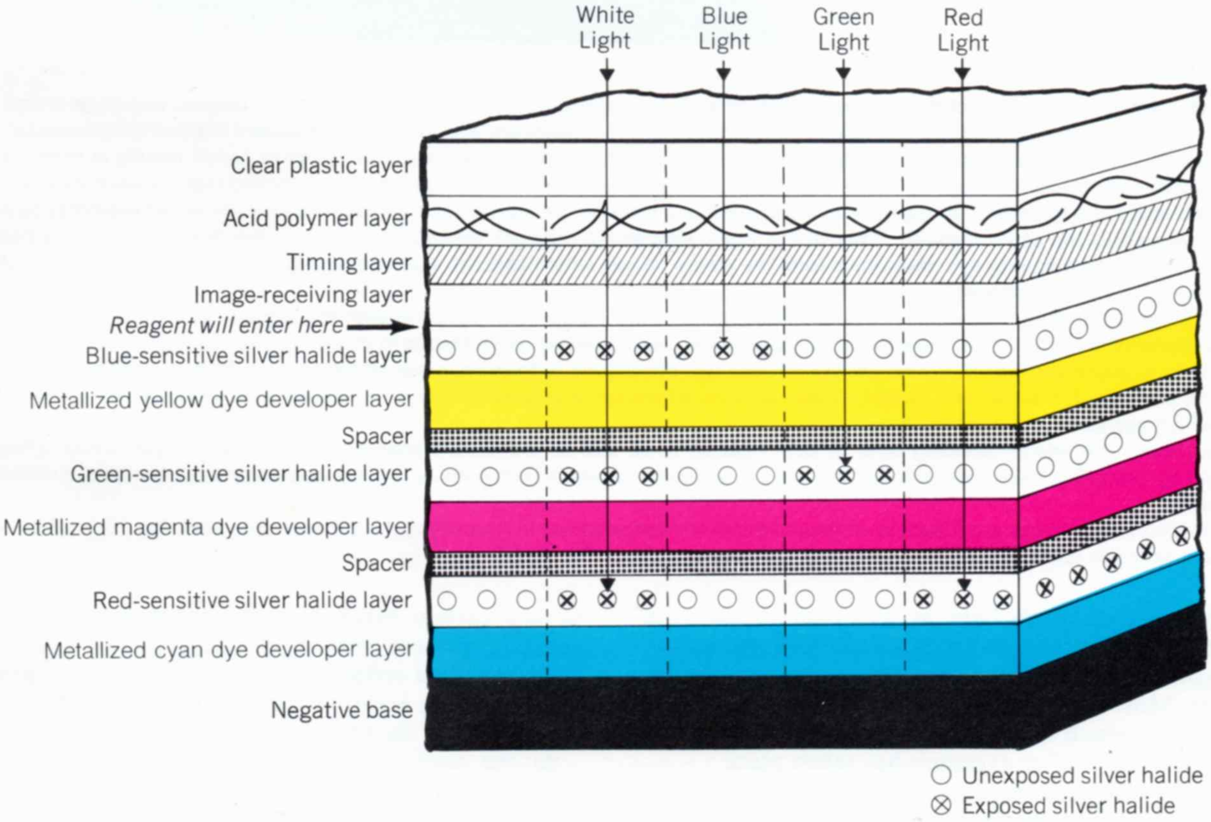

White Light
Blue Light
Green Light
Red Light
Clear plastic layer
Acid polymer layer
Timing layer
Image-receiving layer
Reagent will enter here
Blue-sensitive silver halide layer
Metallized yellow dye developer layer
Spacer
Green-sensitive silver halide layer
Metallized magenta dye developer layer
Spacer
Red-sensitive silver halide layer
Metallized cyan dye developer layer
Negative base
○ Unexposed silver halide
⊗ Exposed silver halide

Fig. 12-9a. Schematic sections of an SX-70 integral film unit during exposure. Color components are metallized dye developers, molecules capable of acting both as photographic developers and as image dyes. Overlying each dye developer is an appropriately sensitized emulsion, which during processing controls the reactions of that dye developer.

Thus the blue-sensitive emulsion controls the yellow dye developer, which, because it absorbs blue light, may also be designated *minus blue;* the green-sensitized emulsion controls the magenta (*minus green*) dye developer; and the red-sensitized emulsion controls the cyan (*minus red*) dye developer. The vertical arrows represent incident light during exposure. The horizontal black arrow at the left of the initial integral structure indicates the interface which will be cleaved and entered by the reagent as it is spread during processing.

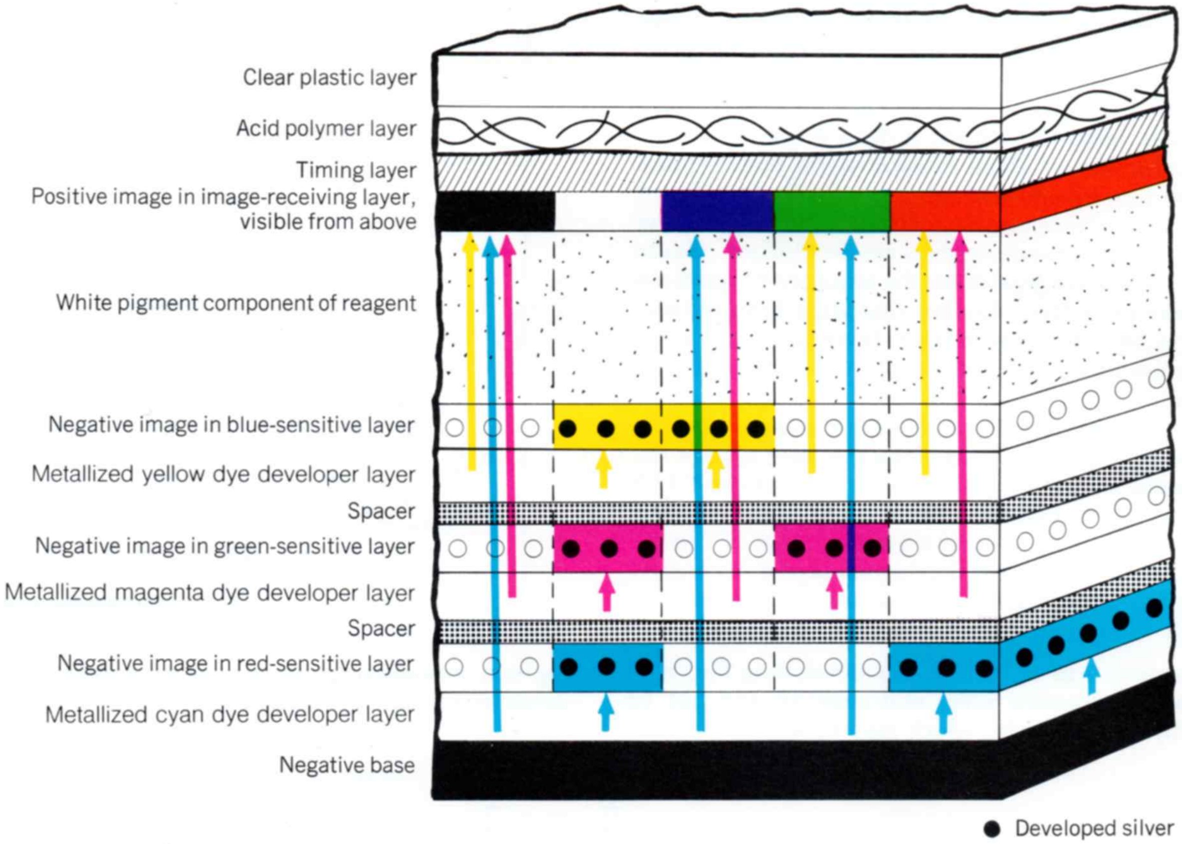

Clear plastic layer
Acid polymer layer
Timing layer
Positive image in image-receiving layer, visible from above
White pigment component of reagent
Negative image in blue-sensitive layer
Metallized yellow dye developer layer
Spacer
Negative image in green-sensitive layer
Metallized magenta dye developer layer
Spacer
Negative image in red-sensitive layer
Metallized cyan dye developer layer
Negative base
● Developed silver

Fig. 12-9b. Schematic section of the integral structure after spreading, with the white pigment of the reagent shown as a new inner stratum. During processing the alkali of the reagent dissolves the dye developers, and each diffuses toward the overlying emulsion layer, as indicated by the colored arrows. In the fully exposed regions of each emulsion, reduction of silver halide results in oxidation and immobilization of the associated dye developer, which therefore remains in the negative. In unexposed regions each dye developer transfers through the emulsion, through the layers above it and through the pigment to the image-receiving layer, where it may be viewed from above against the white pigment. Thus, in the region exposed to red light, the cyan (*minus red*) dye developer is concealed from view; the yellow and magenta dye developers form the visible image, which absorbs blue light and green light but reflects red light and therefore appears red, as shown.

Similarly, green exposure results in immobilization of the magenta dye developer beneath the pigment and transfer of yellow and cyan dye developers to form an image which appears green; and blue exposure results in immobilization of the yellow dye developer beneath the pigment and transfer of magenta and cyan dye developers to form an image which appears blue. In regions of white light exposure, all three dye developers remain in the negative, as shown; and where there is no exposure all three transfer to produce an image which appears black.

Shown above the image-receiving layer in both Figures 12-9a and 9b are the transparent polymeric acid layer, which effects pH reduction by capturing alkali ions, and the timing layer, which by its rate of permeability to alkali ions determines the time of initiation of pH reduction.

The photographic layers are idealized in these figures for convenience in describing the process. See also Fig. 12-3, which shows schematic sections approximately to scale, and the micrographs of Fig. 12-10.

million times as much light as was used to take the picture, unusual protection is required. Both surfaces of the negative within the film unit must be protected from the light. Most important, protection of the negative surface through which the camera exposure is made cannot be provided until after exposure has taken place.

Several configurations were considered for the integral film system. In one, the film unit is exposed through one surface and the image viewed through the opposite surface.* An opacifying layer is brought into position after exposure by application of a processing composition containing carbon black over the exposed surface of the negative, while a preformed opaque carbon black layer, concealed by a reflective white pigment layer,[11] protects the developing negative from exposure through the viewing surface of the film unit.

In the configuration chosen for the SX-70 system, exposure and viewing take place through the same surface of the film unit. Protection of the exposed negative is accomplished by opacifying materials incorporated in the reagent spread to form a layer between negative and image-receiving layers as the exposed film unit passes through the processing rollers. The black polyester negative support protects against exposure of the negative through the opposite surface of the film unit.

*Such a configuration is used in the Eastman Kodak PR10 Instant Print Film introduced in 1976.[12]

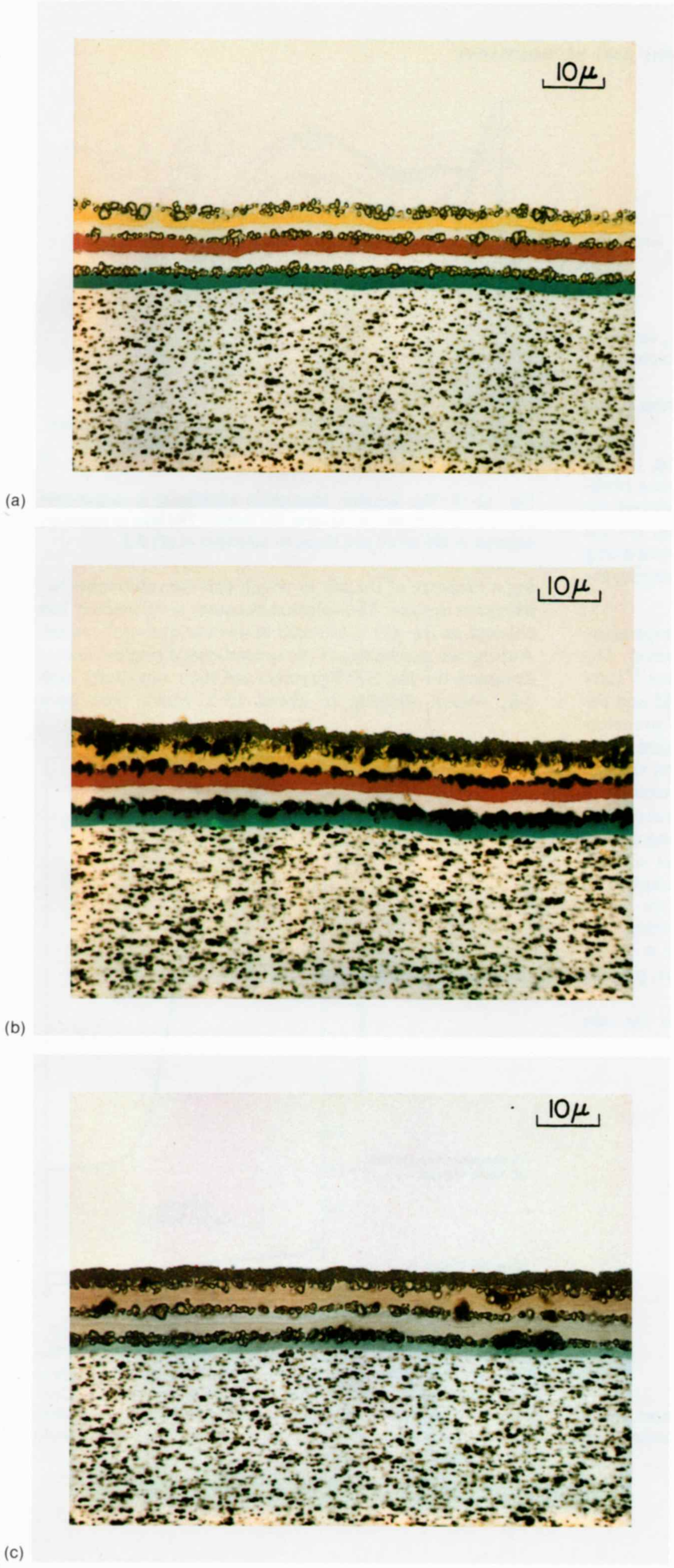


Fig. 12-10. SX-70 negative in cross section, (a) before processing, (b) and (c) after completion of process. Each negative was stripped away from the overlying layers before sectioning. Section (b), from a region of maximum exposure, shows retention of dye developers in the layers of the negative, and Section (c), from an unexposed region, shows only slight residual dye developer. The dark layers at the top surfaces of (b) and (c) are adhered titania pigment; it appears dark by transmitted light.

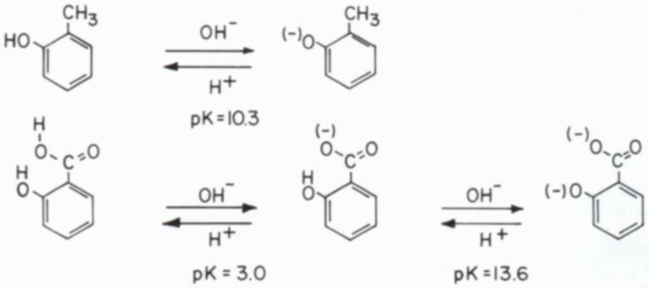


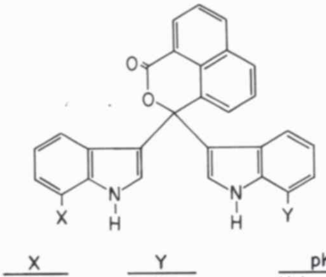
Fig. 12-11. Effect of hydrogen bonding on the pK_a values of phenols. Opacifiers with high pK_a's employ this principle.

In reporting on the SX-70 opacification system, Land said:

> From the point of view of systems planning, the assumption that we could solve this problem was probably our most adventuresome step. We designed the camera as if we had solved the problem, and carried the camera all the way through engineering while doing the basic research on the chemical task of bringing the picture directly into the light.[3a]

A variety of approaches was studied and a large array of opacifying materials examined and synthesized. The method chosen uses a new class of indicator dyes[10b] having high absorption coefficients at very high pH and becoming colorless and remaining colorless at predetermined lower pH. The indicator dyes are included in the viscous reagent, rendering it opaque when first spread. Shortly after spreading, as pH is reduced by the capture of alkali ions in the polymeric acid layer, the indicator dyes become colorless. The success of this opacifying system made it possible to build a camera without a dark chamber* and to build a film pack of great simplicity.

The opacifying indicators are phthalein dyes which react in the same manner as familiar pH-indicating dyes of this class. A solution of such an indicator is highly colored when the dye is at or above its pK_a value, pK_a being a measure of the pH at which half the removable hydrogen is ionized. The solution becomes progressively less colored as the pH is reduced below the dye's pK_a value. Among the properties of the special opacifying indicators designed for the SX-70 system are their unusually high pK_a values, ranging to about 13.5, which have been



X	Y	pKa
H	H	11.1, 13.8
CO_2H	CO_2H	13.2, > 15
CO_2H	$-NH\,SO_2C_{16}H_{13}$	12.9, > 15
CO_2H	$-SO_2NH\,C_{18}H_{37}$	12.9, > 15

Fig. 12-12. A series of naphthalein opacifying indicators, showing the increase of pK_a value by use of hydrogen bonding substituents in positions X and Y.

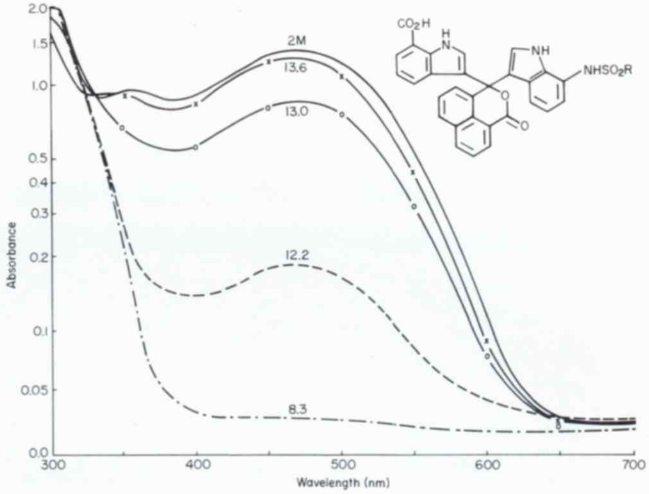


Fig. 12-13. The solution absorption spectra of a naphthalein opacifying indicator at several pH levels. The dye is intensely colored in 2M alkali and close to colorless at pH 8.3.

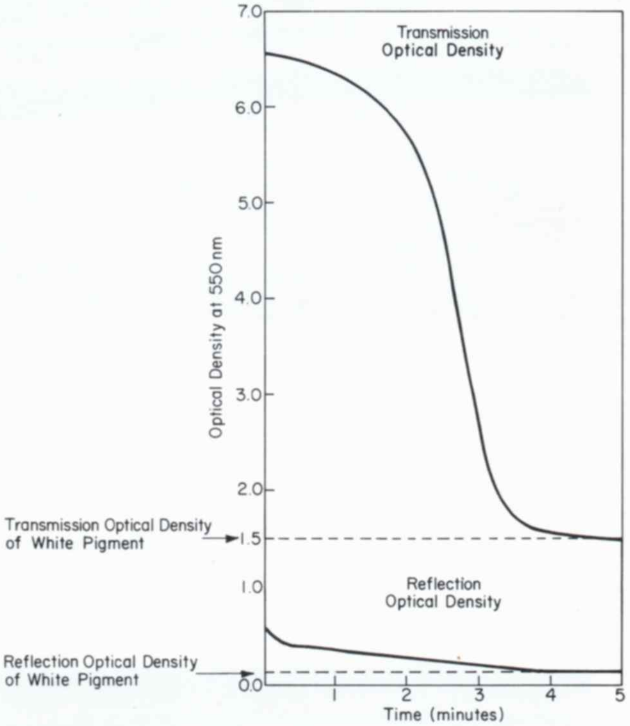


Fig. 12-14. Transmission and reflection densities of the opacifying reagent system plotted against time after spreading. The two curves together show that the reflectance from the front is high even when the transmission is very low indeed. Consequently the dyes in the image-receiving layer are seen against a background adequately light for the image to be visible while the negative is still protected.

*Compact cameras also have been designed for integral film units which do not have such an opacification system.[13]

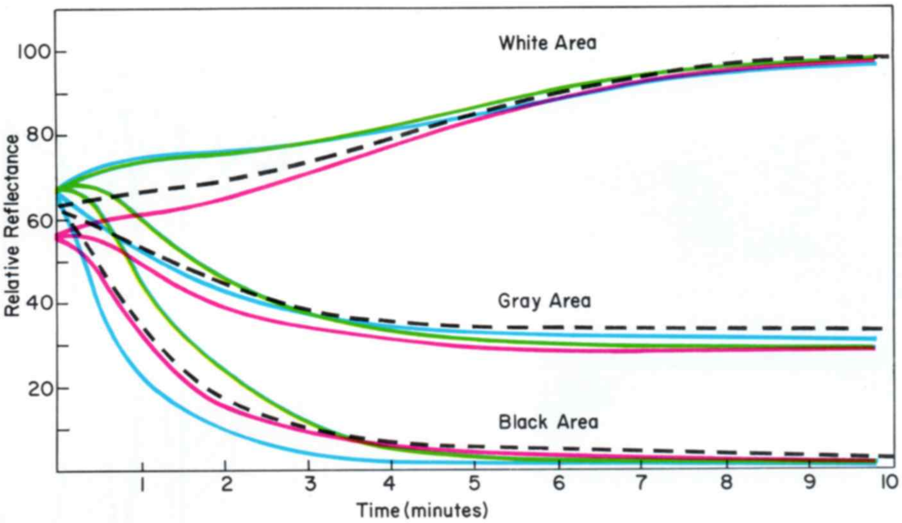


Fig. 12-15. Materialization of SX-70 image in white, gray and black areas. The opacifiers lose their color as pH is reduced by capture of alkali in the polymeric acid layer, and dye images continue to intensify. The color curves show the change of relative red, green and blue reflectances with time, and the dotted black curve indicates reflectance observed visually.

achieved by introducing hydrogen bonding groups into the dye molecule in juxtaposition with the removable hydrogen. Figure 12-11 illustrates the effect of hydrogen bonding on the pK_a of phenols, and Fig. 12-12 shows the increase of pK_a values of a naphthalein opacifying indicator by means of hydrogen bonding substituents.

A very high concentration of alkali is thus required to free the hydrogen ions and to produce the highly colored form of the indicator. This principle is demonstrated by the solution absorption spectra of a naphthalein opacifying indicator, Fig. 12-13, at several pH levels. The indicator is highly colored in 2 molar alkali and close to colorless at pH 8.3. Additional important properties of the opacifying dyes are their stability over prolonged periods in the highly alkaline environment of the reagent prior to processing and their spectral absorption in the colored state appropriate to provide protection to the negative.

Opacification is achieved by a synergistic optical effect of the opacifying dyes and the titanium dioxide pigment. Mixing the dyes with the highly reflective titania pigment greatly extends the path length of light passing through the layer, thus increasing the amount of light absorbed by a given quantity of dye.

Figure 12-14 shows the transmission and reflection densities of an SX-70 opacification system at 550 nm as a function of time following the initiation of processing. The transmission density, which is a measure of the light passing through the reagent layer to the negative, is initially over 6.5, so that the amount of light incident upon the negative is less than a millionth of the ambient level when the developing film unit exits the camera. Because of the high reflectivity of the pigment, the *reflection* densities are low throughout the process and the transferring SX-70 image becomes visible against the pigment before the opacification system has been fully decolorized.

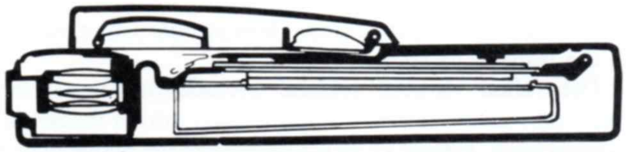


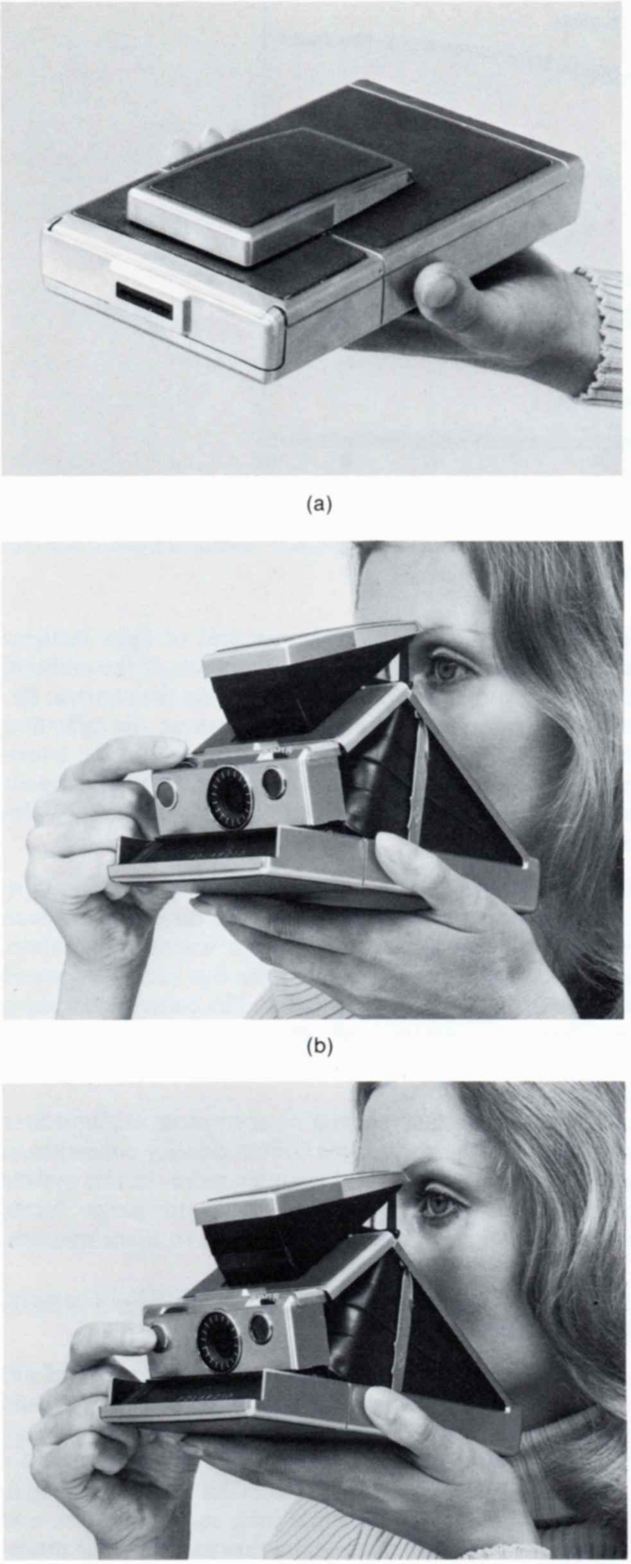
Fig. 12-16. Cross section of SX-70 camera in closed position, with outline of film cassette in place. Both the viewer assembly and the lens-shutter assembly are articulated so that the camera can fold flat.

Image Materialization. Figure 12-15 shows the concurrent changes of red, green and blue reflectance in each of three picture areas, areas which will become white, gray and black, respectively, as the dye image is formed and the opacifiers lose their color. The color curves show the change in relative red, green and blue reflectances with time, and the dotted black curve indicates reflectance observed visually.

The gray area has reached its asymptote in about four minutes, and the area of maximum density continues to grow in density for several minutes more. In this system pictures become sufficiently visible to judge focus, exposure and composition within one to three minutes.

The SX-70 Camera. In introducing the SX-70 camera, Land commented:

> In retrospect I notice that within the framework of our overall objective, in which camera and film would cooperate, the camera concept and the film concept took on independent individuality. We dreamed of a camera, and even designed one, that would not have to open at all to take a three inch square picture, and which would, nevertheless, be thin and flat. The model we have demonstrated does indeed open from a flat position, so simply and so directly and to a shape so appealing, that we quickly adopted it. Fortunately, we had trouble finding a good place for the viewer. We solved the problem by realizing that the very special shape of the camera lent itself to the design of an equally unusual single lens reflex viewer.[3a]



(a)

(b)

(c)

Fig. 12-17. (a) SX-70 camera in closed position; (b) photographer adjusts focus with forefinger while viewing subject through the single lens reflex viewer. Electric trigger button is just below forefinger. (c) Photographer presses trigger to expose film; developing film unit is ejected from the camera within 0.4 sec after the shutter closes.

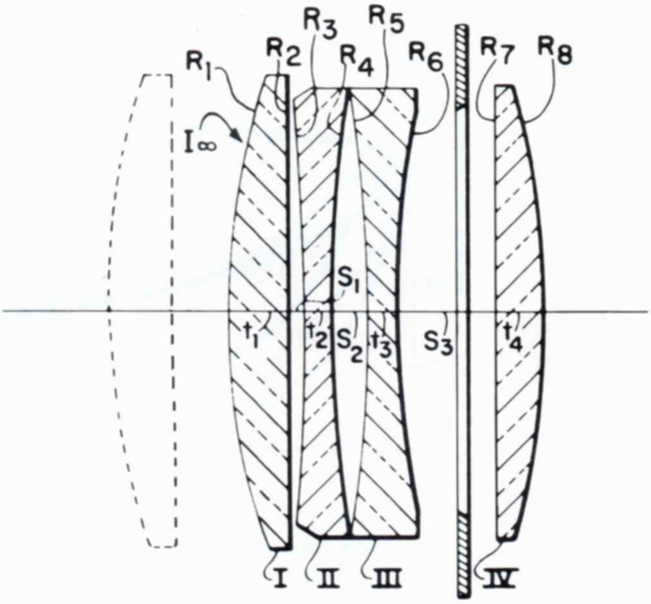


Fig. 12-18. Diagram of SX-70 lens design, a patent illustration.[14a] The dotted outline at the left indicates the furthest extension of the front element. Total travel of the front element to focus from infinity down to 10 in. is 0.23 in., and the total distance from front to back when the front element is fully extended is 0.67 in. The compact design permits the camera to be closed even when the lens is fully extended.

Folding the light path between lens and film with a mirror permitted a longer focal length lens for a given size film, and a mirror led to a more compact camera. Using the mirror provided two principal advantages. The first was that it reversed the image laterally, thus meeting the requirements of the new pack for a laterally reversed image.* The second advantage was that it facilitated a compact design for a folding camera. A radically new assembly including new lens, new shutter, new diaphragm, new focusing, new electromechanical control, new solid state electronics, conceived as a unitary design, made possible an extremely compact lens-shutter housing; this compact housing made it feasible to take full advantage of the folded light path.[6] All this made possible a camera for a large image, compact enough and light enough (about a pound and a quarter) to be carried in a coat pocket or purse, as shown in Figs. 12-16 and 12-17a. Figures 12-17b and 12-17c show the camera in use.

Baker's singular lens design[14a] is shown in Fig. 12-18. The *f*/8 lens, which is focused by displacement of the front element, operates at front focal distances from infinity all the way down to 10 in. Its focal length is 116 mm. The total length of the lens is only one-eighth of its focal length. A simple auxiliary lens provides for closeups in the range 5 to 10 in.

The reflex viewing system[4] includes a hinged decentered Fresnel mirror [14b] and a fixed mirror inside the camera back. Figure 12-19 is a schematic ray diagram and

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*Integral films providing exposure through one surface and viewing of the image through the opposite surface, as described on page 266, do not require laterally reversing mirror optics.

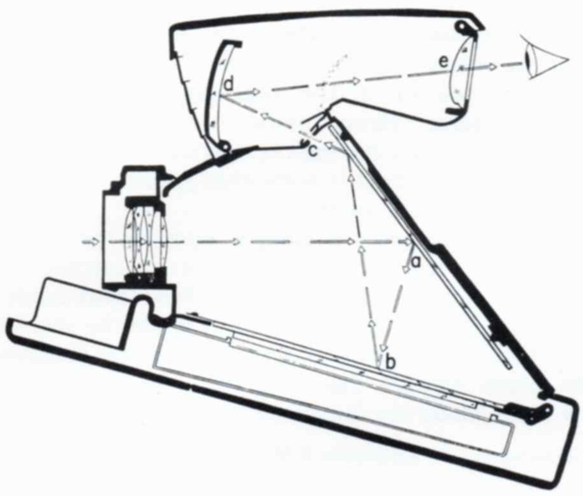

Fig. 12-19. Path of rays in viewing mode. The rays pass through the lens to the permanent mirror (a) on the sloping face. They are reflected from this mirror downward toward the image plane, where they strike the surface of a decentered front surface Fresnel mirror (b), are directionally reflected by the Fresnel upward for a second reflection from mirror (a), pass through a tiny aperture (c) at the top of the camera, strike an aspheric concave decentered mirror (d), and pass through the aspheric decentered eyepiece (e) to the eye; all rays through the lens to the image plane meet with an analogous fate, and all converge behind the pupil of the eye. The concave mirror forms an image of the focal plane about the size of a small postage stamp about one-half of the way between the eyepiece and the concave mirror (dotted line).

The surface of the Fresnel mirror is roughened to form a focus screen, so that the eye receives light originating from the entire area of the taking lens as with a conventional ground glass focus screen. The roughness of the Fresnel is carefully controlled; it is made sufficiently rough to prevent the eye from accommodating to an incorrectly focused image and to include light from the margin of the lens, but still not rough enough to make the image dark. This compromise can be arranged so that the relative focusing effectiveness and the relative brightness are both above 84%.

The single-lens reflex system enables the photographer to frame and focus accurately using the full area of the focus screen at ordinary light levels. To assist in focusing under low light level conditions, the focusing screen includes a split image range finder. The photographer sees the range finder as a small circular region slightly below the center of the screen, crossed by a horizontal division line. When the camera is being focused, the parts of the image above and below the division line move in opposite directions, and they match only when the camera is focused correctly. The range finder, which replaces a small circular portion of the Fresnel mirror, comprises two Fresnel sections that have been decentered. Decentering these small pieces of the focusing screen is optically equivalent to tilting them, and the split image behavior is thus equivalent to that produced by a pair of thin prisms in a conventional reflex camera.

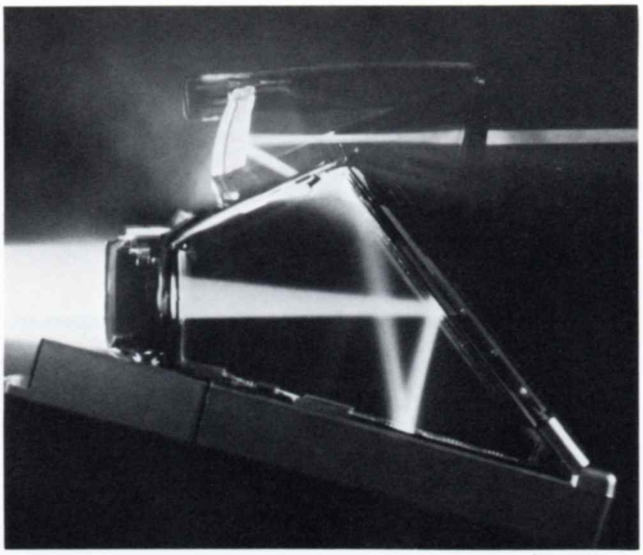

Fig. 12-20. "Smoke box" picture of ray paths through the SX-70 camera in viewing mode.

Fig. 12-20 a "smoke box" picture of the ray paths during viewing. In the viewing mode the Fresnel overlies and shields the film units, as shown in Fig. 12-19. When the electric trigger is touched, the Fresnel mirror swings up to rest upon the permanent mirror, as in Fig. 12-21. The other side of the Fresnel carries the taking mirror. Before the Fresnel moves, the shutter will have been closed electronically. It will open again to take the picture when the taking mirror is in place. Light rays passing through the lens are now reflected by the taking mirror to the film in the focal plane. After the correct exposure the shutter will close, the taking mirror and the Fresnel will return to their positions covering the film pack, and the shutter will return to the open position for viewing. Within a fraction of a second after the shutter closes, the top film unit is ejected through the motor-driven rollers and the whole cycle of picture taking is ready to be repeated.

The SX-70 camera itself contains no batteries, the motor, the shutter and the electronics drawing their re-

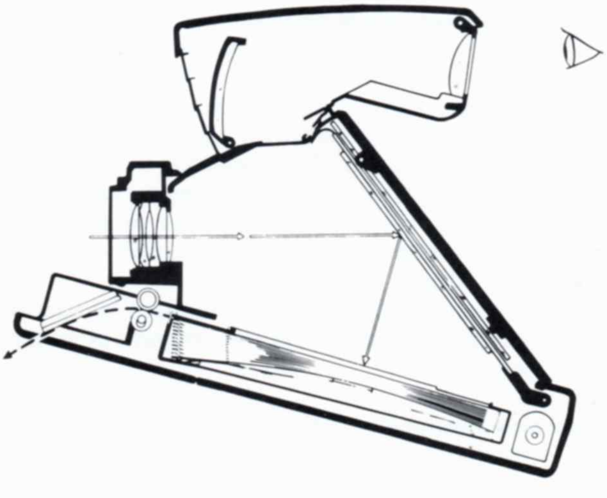

Fig. 12-21. Path of rays in taking mode. Pressing the trigger raises the hinged unit carrying the Fresnel, occluding the viewing mirror and presenting the taking mirror. Light entering the camera through the lens strikes the taking mirror and is reflected downward to the uppermost film unit. After exposure the film unit will follow the path indicated by the dotted line between the rollers and out of the camera. See also Fig. 12-23c.

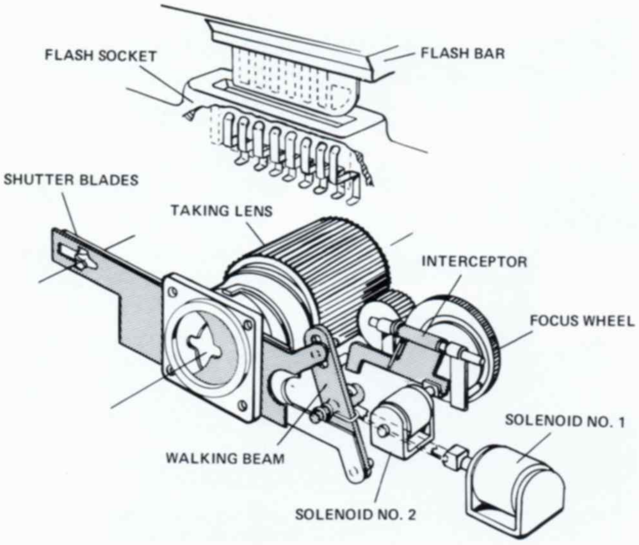

Fig. 12-22. Follow-focus system for flash exposure. The follow-focus circuit is put into service by the insertion of the flash bar. Solenoid No. 1, the principal shutter solenoid, drives the shutter blades. The blades are opened and closed at a predetermined speed; thus exposure is a function of aperture. Solenoid No. 2 puts the interceptor into operating position, and the interceptor pin determines the maximum travel of the walking beam during exposure; the walking beam, in turn, determines the maximum aperture reached by the shutter blades.

quired power from the battery in the film pack. Integrated circuits control all the operations of the camera and automatically determine the exposure when the electric trigger is touched. The shutter blades, shaped to define the lens aperture, are opened and closed by the action of an electronically controlled solenoid.

In available light photography the system operates in the integrating mode, using as light sensor a tiny photodiode. The surface area of the photodiode is less than .006 in.^{2} (4 mm^2), and it generates extremely small currents (10^{-12} to 10^{-9} amp). During exposure, light sensed by the photodiode generates a current which charges a capacitor to a predetermined level. When the capacitor reaches that level it discharges and its circuit instructs the solenoid to close the shutter blades, thus terminating the exposure. If the light level is too low to charge the capacitor sufficiently, the shutter is closed automatically after approximately 20 sec.

The following table shows combinations of aperture and shutter speeds included in the program of ambient light exposures:

Average Scene Luminance (candles/ft^2)	Equivalent *f*/Number	Effective Shutter Speed (sec)
800	22	1/180
400	16	1/140
200	14	1/120
100	11	1/90
50	8	1/70
25	8	1/35
12	8	1/18

For short exposure times the equivalent *f*/number is held during only a very small fraction of the time, so that a significant portion of the total exposure occurs at smaller apertures. Hence motion-stopping ability is somewhat better than that indicated by the total exposure time, and depth of field is somewhat greater than that indicated by the peak aperture.

When the flash array is plugged into the top of the shutter housing the circuitry converts exposure control from the integrating mode to the follow-focus mode, illustrated in Fig. 12-22. Once in this mode the shutter speed is fixed and aperture is determined by the position of the focus wheel.* The programmed exposures in follow-focus mode are illustrated in the following table.

Distance to Subject	Equivalent *f*/Number	Shutter Speed (sec)
10.4 in.	96	1/40
12.0 in.	90	1/40
3.0 ft.	32	1/40
6.0 ft.	19	1/40
15.0 ft.	9	1/40
20.0 ft.	8	1/40

The flash control circuit chooses from the five bulbs in each side of the linear flash array the next to be ignited, and prevents firing when it senses that the film pack is empty. The circuit also prevents firing of a flashbulb during ejection of the dark slide when the camera is being loaded with a new pack of film.

Further functions of the electronic circuitry include the control of the mirror action, the automatic ejection of the dark slide after the film pack is inserted into the camera, as in Figs. 12-23a and 23b, and the command of the motor action which passes the film unit between processing rollers and out of the camera, as shown in Fig. 12-23c. In addition there is an electronic brake which brings the motor from 13,000 rpm to a standstill in less than 10 revolutions. The substitution of electronic control and switching for mechanical elements, plus the thin lens design,[13] make possible the compact shutter housing.

The result of the new technology in film, camera and process was a system which could readily establish the direct relationship set forth as a goal in the earliest work—the relationship between subject, photographer and finished picture. The simple, automatic operation of the SX-70 makes possible a wide range of new applications in both general and technical photography.

Scope of One-Step Photography

Land's report on the SX-70 system marked the introduction of a greatly advanced photographic medium in a field

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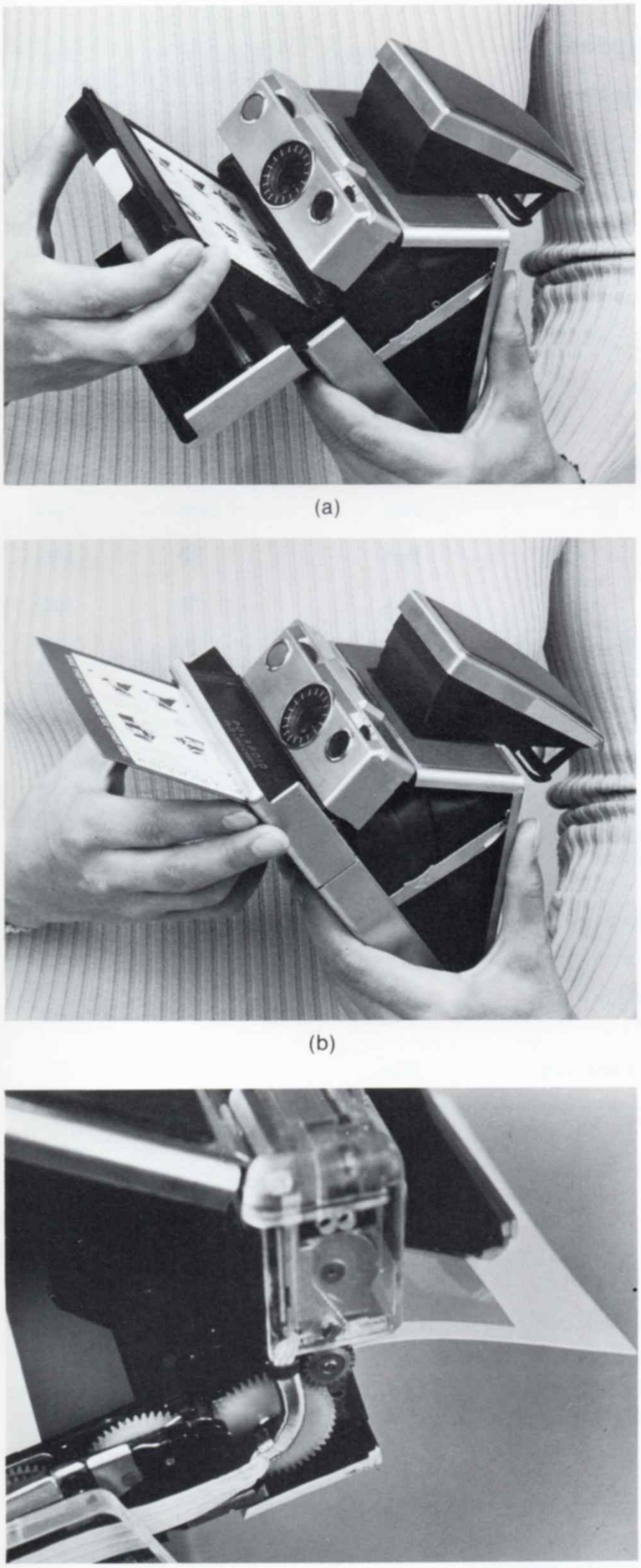
*In the later SX-70 cameras integrating exposure control is superimposed on the follow-focus mode, so that when flash is used, after aperture has been determined by the focus wheel position, the electric eye monitors the scene and closes the shutter as soon as it has received sufficient light. This combined control system makes the focusing less critical and helps to compensate for scene brightness variations.


(a)

(b)

(c)

Fig. 12-23. (a) Film pack being inserted into camera; (b) automatic ejection of cover sheet after film pack is inserted; (c) ejection of film unit following exposure, photographed in cutaway camera model as seen from the side opposite that shown in (a) and (b).

already characterized by innovation and rapid growth. In its first 25 years, one-step photography had grown from a laboratory achievement into an industry which accounted for a significant fraction of both amateur and professional photography.

One-step processes had been introduced for black and white photography and for color photography, first in roll film cameras which completely processed the film inside the camera,[15] later in packet holders[16] and pack[17] and roll film[18] cameras permitting processing outside the camera. The materials introduced during this period include films for black and white prints, color prints, transparency films, films of ultrahigh speed, films for X-ray and for infrared, and professional positive-negative film.* At the end of 1976, 7.2 billion black and white pictures and 5.7 billion color pictures had been made with these materials by users of more than 62 million cameras. More than 1.4 billion of these prints were made in 1976, and over 68% of the 1976 pictures were in color.

Simultaneous observation of an object and its photographic record is widely recognized as a powerful tool for workers in a variety of scientific, educational and industrial fields. Polaroid one-step processes and cameras have been adapted to many laboratory instruments; in some fields of laboratory science the whole method of operation has been radically changed by utilizing the flexibility and immediacy of the photographic result. Polaroid one-step cameras are standard accesories in microscopy and oscillography, and in many cases they are integral parts of such instruments as scintillation cameras, scanning electron microscopes, photoelastic stress analyzers and infrared microscanners. Figure 12-25 outlines major technical applications, and examples of results are shown in Figs. 12-26 and 12-27.

EVOLUTION OF ONE-STEP PHOTOGRAPHY

Initial Specifications

When, in 1943, Land undertook the design of one-step systems to produce pictures which could be viewed immediately after taking them, he set the following specifications: a hand-held camera would yield finished pictures instantaneously, replacing the many time-consuming steps of classical wet process photography. Film speed would be high enough to permit hand-held pictures at modest lens apertures. The processing, to be practical for incorporation in a camera, needed to be dry or apparently dry. The system had to operate effectively over a temperature range extremely wide compared with the range useful in ordinary darkroom processing. The pictures had to be of suitable size and quality for direct viewing. Film, process and camera

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*Figure 12-24 lists all Polaroid films for reference. Representative films will be further described in the discussions of one-step mechanisms in later sections.

Picture	Film Type*	Special Purposes and Characteristics	Spectral Sensitivity	Equivalent ASA Speed**	Date of Introduction
Sepia	*40*		*Ortho*	*100*	*1948*
Black and White	*41, 31*		*Ortho*	*100*	*1950*
	42 (Polapan 200)		Pan	200	1955
	32, 52		Pan	400	1955
	43, 53 (Professional Pan)	*Negative on transparent base*	*Pan*	*200*	*1955*
	44 (Polapan 400)		*Pan*	*400*	*1955*
Normal Contrast Range for Continuous Tone	47, 37, 57, 107, 20, 084 (Polaroid 3000)	High speed films	Pan	3000	1959
	87, 20C, 107C, 667	Coaterless	Pan	3000	1970
	55 P/N (Professional Positive/Negative)	Positive plus fixed negative	Pan	50	1961
	105 P/N		Pan	75	1973
	1001	X-ray films: TLX is provided on translucent base for viewing by transmission or reflection	*Ortho*	*100*	*1952*
	1001		Pan	200	1958
	3000X		Pan	3000	1961
	TLX		Ortho	1500	1966
	413 Infrared Film		*Infrared*	*800*	*1965*
High Contrast	410 (Polascope)	Very high speed for rapid oscillography and halftone	Pan	10,000	1961
	510		*Pan*	*10,000*	*1964*
	51	Medium speed for halftone	Blue	320	1967
Black and White Trans-parency	*46*, 46L	Normal contrast for continuous tone	Pan	800	1957
	146L (Polaline)	High contrast for line copy	Blue	200	1961
Color	*48, 38, 108, 58, 88, 636 (Polacolor)*		*Daylight*	*75*	*1963*
	SX-70		Daylight	150	1972
	108, 88, 58, 668 (Polacolor 2)		Daylight	75	1975

*Film Type denotes format, as well as photographic characteristics:

"40," "30" and "20" series are roll films, for picture sizes 3¼″ x 4¼″, 2½″ x 3¼″ and 2½″ x 3¼″, respectively (including border).

46 and 46L refer to square and lantern slide format transparencies, picture areas 2¼″ x 2¼″ and 2 7/16″ x 3¼″, respectively.

"50" series are packets for use with 4″ x 5″ Film Holder; picture area 3½″ x 4½″.

"100" and "80" series are pack films for picture sizes 3¼″ x 4¼″ and 3¼″ x 3⅜″, respectively (including border).

1001, 3000X and TLX are packets for use in 10″ x 12″ X-ray cassettes; picture area 9⅜″ x 10½″.

SX-70 integral film units are 3½″ x 4¼″ overall, with picture area 3⅛″ x 3⅛″.

Italics: Discontinued

**ASA standards have not yet been established for Polaroid one-step films. "Equivalent ASA speed" indicates the exposure index to which a meter calibrated in ASA speed units should be set for proper daylight exposure.

Fig. 12-24. Polaroid films.

Visible Signal From Subject Photographed Directly

- Photoelastic Stress Analysis Units
- Plano Interferometers
- Laser Energized Interferometers
- Thin Film Interferometers
- Emission Spectrographs
- Monochromators
- Fabric Control Cameras for Clothing Patterns
- Sequencing Cameras
- Photomicrographic Cameras
- Fundus Camera for Retinal Photography[19a]
- Keratoscopes for Plotting Contours of the Human Eye
- Field Plotting Units for the Human Eye
- Extra-Oral Dental Cameras
- Immunodiffusion Cameras
- Endoscopes[19b]

Non-Visible Signal Converted to Light for Recording on Film

- Oscilloscopes
- Scanning Electron Microscopes
- High Speed Image Converter Cameras
- Interval Timer-Recorders for Seismography
- Digital Print Recorders
- Thermographic Scanning Units
- Ultrasonic Scanners for *in Vivo* Testing
- Scintillation Cameras for Nuclear Medicine
- Spirometers for Pulmonary Function Testing
- Electromyograph Recorders

X-Ray Images Recorded on Film

- Portable X-Ray Generators for Radiographic Analysis
- Crystallographic Orientation Cameras[19c]
- Cassette Processor for Medical and Industrial X-ray[19d]

Fig. 12-25. Major industrial and scientific applications of one-step photography, utilizing specialized film holders and cassettes, integral camera backs or special purpose cameras. Camera backs include both pack and roll-film models. Special purpose Polaroid Land cameras include the MP-3 and MP-4 industrial view cameras, the CU-5 close-up camera, the CR-9 oscilloscope camera, the ED-10 instrument camera, and the ID-2 identification camera. Since the literature in some of these fields is extensive, only representative papers and bibliographic references have been noted. Reference 20 is a periodical devoted to technical applications. Further references and detailed information are available through the Polaroid Corporation's technical staff and from manufacturers of the specific instruments.

evolved as a chain of consequences of this set of photographic precepts.

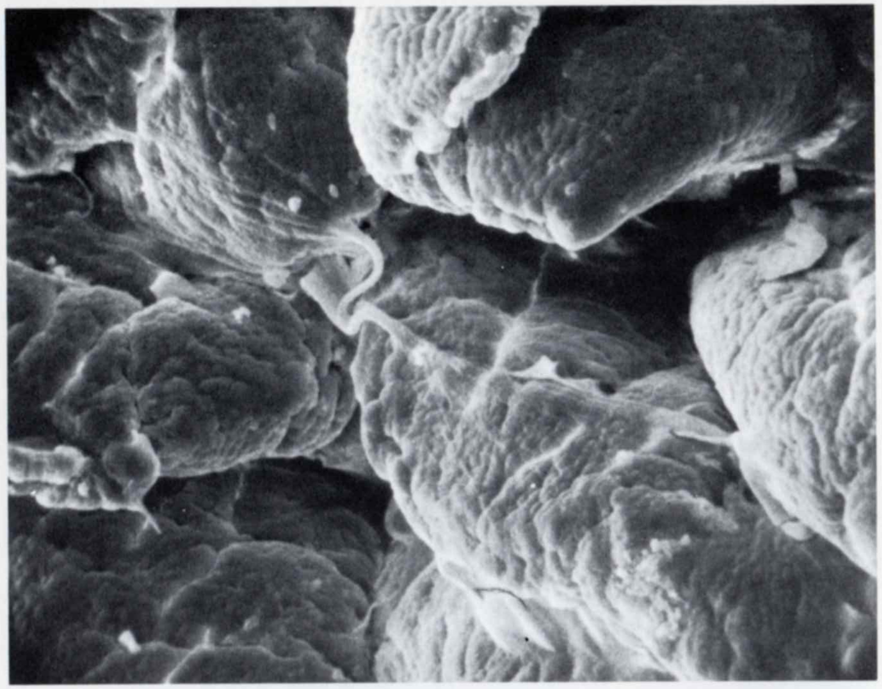
The Photosensitive Material. Silver halide was the photosensitive medium preferred for a hand-held camera process because of its high sensitivity to light and the extraordinary amplification of the latent image by development. For uses other than a hand-held camera a variety of photosensitive systems could be considered seriously; for the sensitivity required in a hand-held camera the only candidate was silver halide. Given a silver halide emulsion as starting material, the task was to exploit during the course of development the difference between exposed and unexposed silver halide grains as a means of forming a final positive image. The positive image could be of dye, of silver, or of the two in combination.

Reference 2 points out that the treatment of an exposed emulsion with a developer containing conventional components initiates a series of reactions which vary from point to point as a function of exposure. Each reaction thus produces a set of images in terms of materials consumed or altered and a corresponding set in terms of unreacted materials.

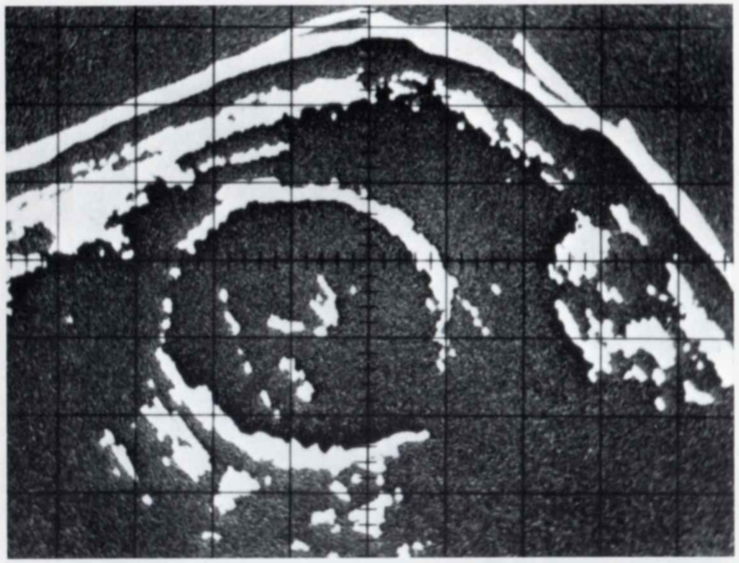
Thus we can tabulate a series of "images," many of them invisible, and such a table is shown below*. . . . Most of these ten images are chemical types, and each of the images is a candidate for being instrumental in forming the positive. The odd numbered images are associated with the highlights in the original scene, and the even numbered with the shadows. Therefore, in making the positive, the odd must either do nothing with relation to a white surface or else whiten a black surface. The even must either do nothing to a black surface or else blacken a white surface.

In conventional tank or tray development of negatives and prints, the image comprising exposed grains is converted to a final image of developed silver. None of the other images listed in the table is used. In one-step processes, as in certain of the multistep reversal processes, it is possible to utilize many of the other images, including those which are soluble. If the system transfers an image to a separate sheet or a separate layer, it may make effective use of each of those shown in the table, either alone or in combination.

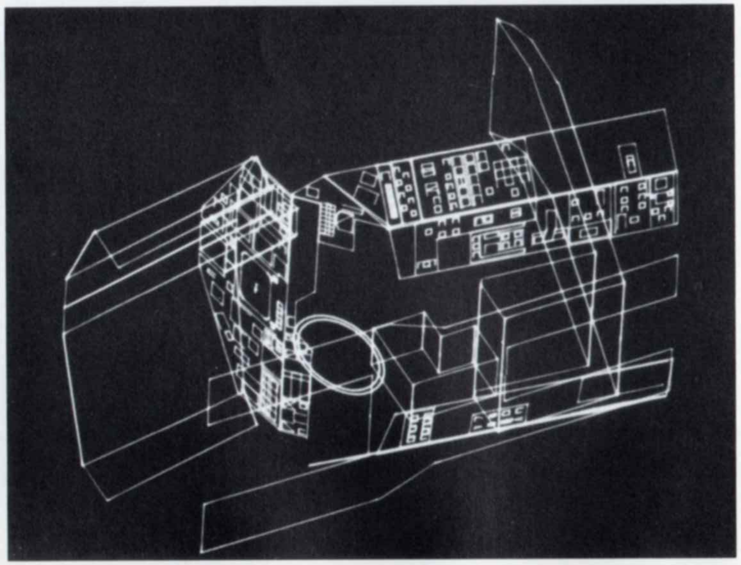
*Figure 12-28 reproduces this table (page 280).



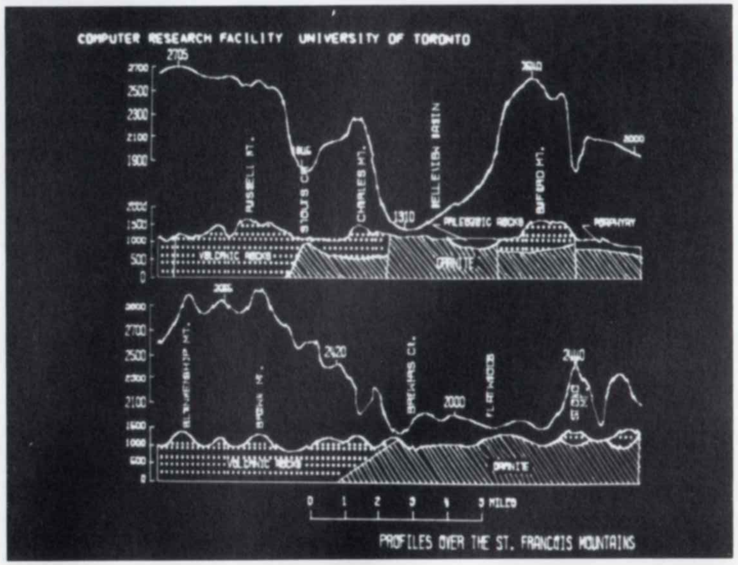
(a)



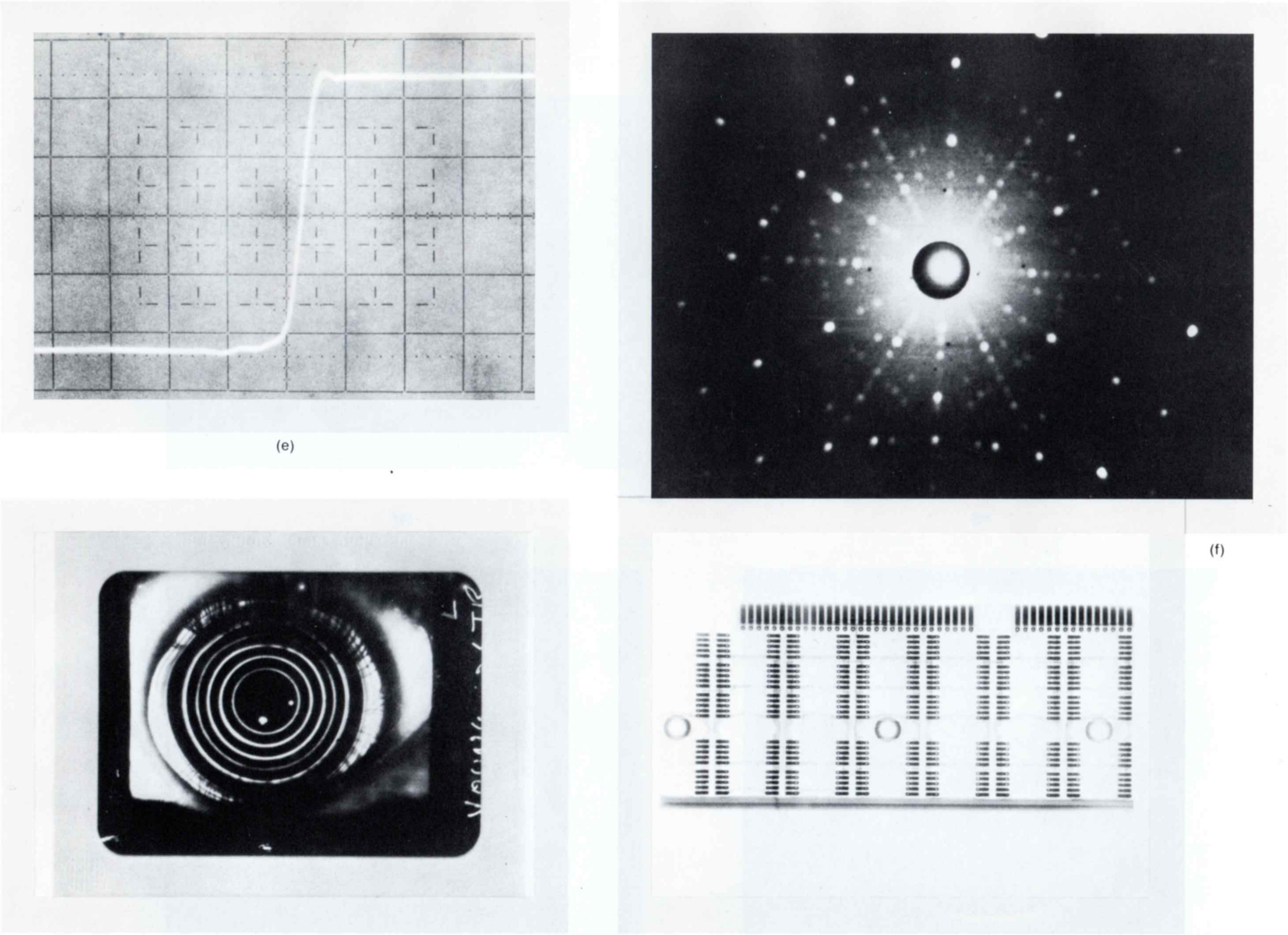
(b)



(c)


COMPUTER RESEARCH FACILITY UNIVERSITY OF TORONTO
2705
2700
2500
2300
2100
1900
RUSSELL MT.
STOUTS CR.
CHARLES MT.
1310
BELLEVIEW BASIN
BUFORD MT.
2000
PALEOZOIC ROCKS
PORPHYRY
VOLCANIC ROCKS
GRANITE
2000
1500
1000
500
0
2700
2500
2100
1600
1000
600
0
2420
BREWERS CT.
2000
2410
VOLCANIC ROCKS
GRANITE
0 1 2 3 4 5 MILES
PROFILES OVER THE ST. FRANCOIS MOUNTAINS

(d)


(e)

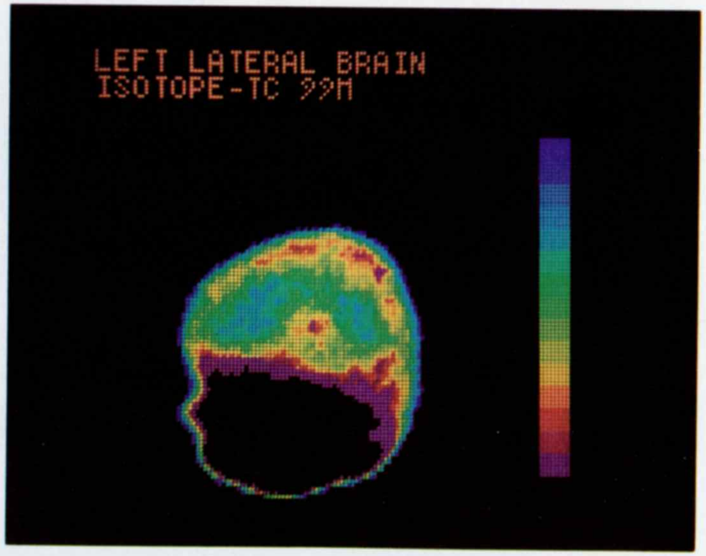
(f)

(g)

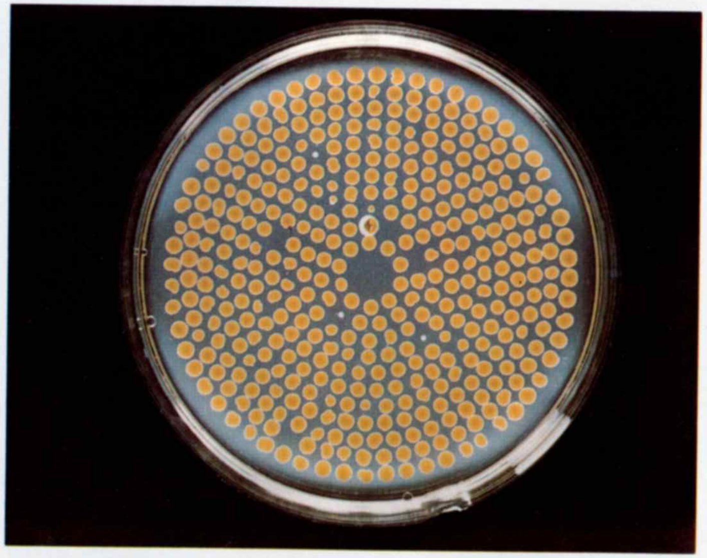
(h)

Fig. 12-26. Technical applications of one-step photography. Film type is indicated in parentheses:

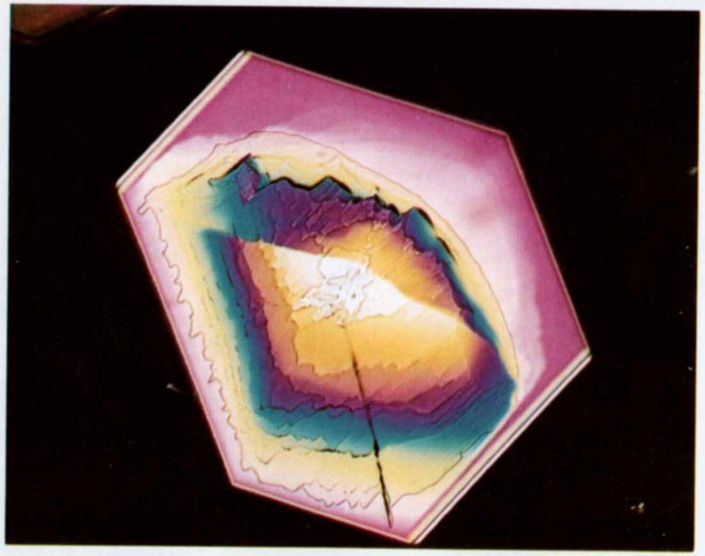
(a) Scanning electron micrograph, villi of rat intestine (Type 55 P/N);
(b) Ultrasonic scan of fetal skull *in utero* (Type 107, speed 3000);
(c) and (d) Computer-generated oscillograms (Type 107, speed 3000);
(e) Rapid oscillographic trace, 5 nsec/division (Type 410, speed 10,000);
(f) X-ray diffraction pattern, Al_2O_3 (Type 55 P/N);
(g) Keratoscope contour plot of human eye (Type 46L);
(h) Radiograph of multilayer printed circuit (Type 52).



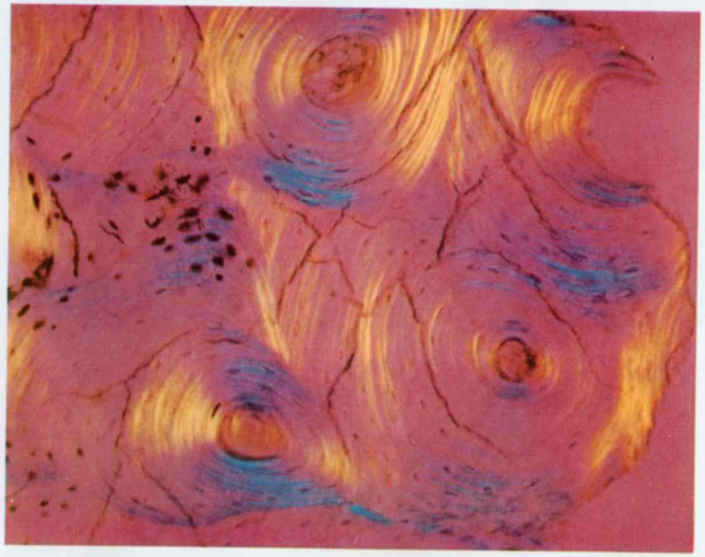
(a)



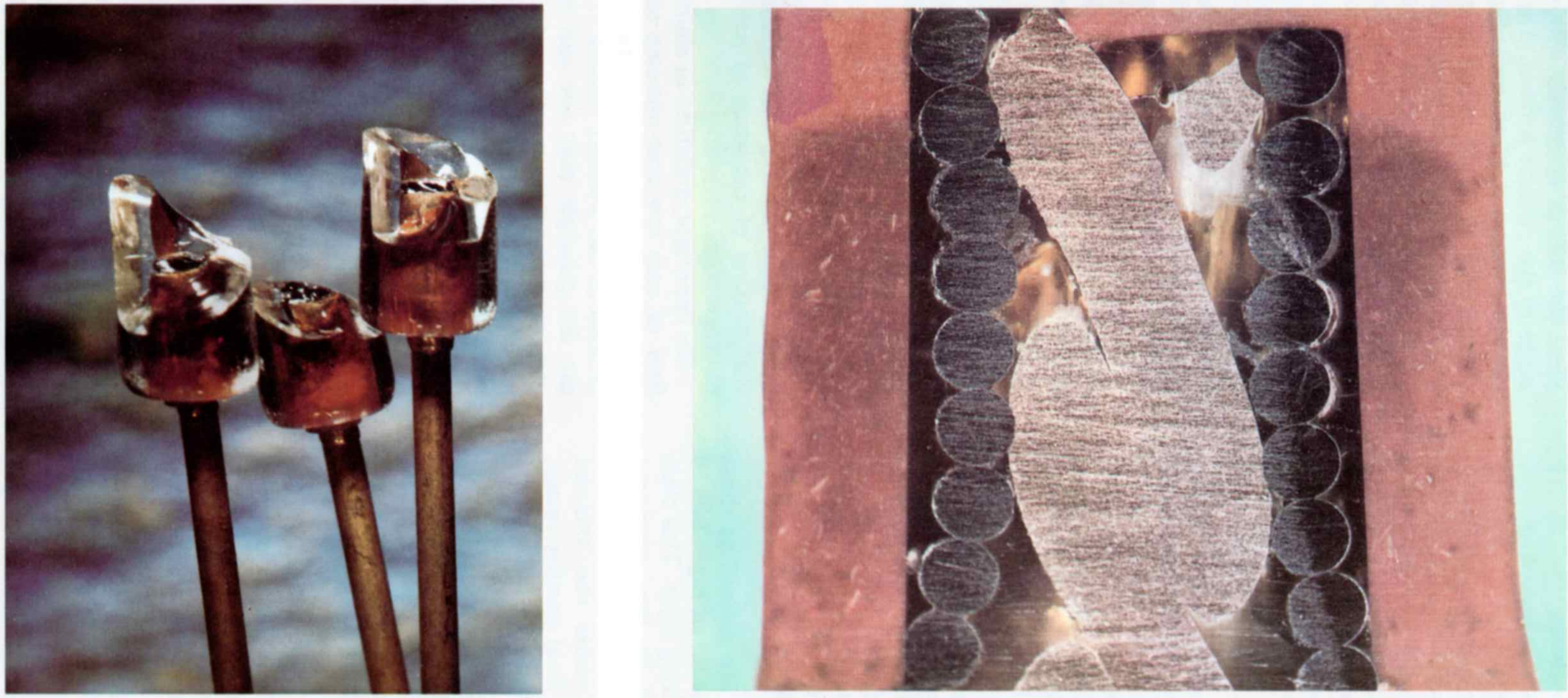
(b)



(c)



(d)



(e) (f)

Fig. 12-27.

(a) Scintillation camera record, human brain following uptake of a radioactive isotope. Digital count data is color coded by computer, then displayed and photographed in color to facilitate diagnosis (Type 108);
(b) Macrophotograph (original 1/3X), bacterial colonies (Type 108);
(c) Micrograph (original 200X), aspirin crystal between crossed polarizers (Type 108);
(d) Micrograph (original 120X), section of diseased bone between crossed polarizers with sensitive tint plate (Type 108);
(e) Macrophotograph (original 10X), fractured diodes (Type 58);
(f) Macrophotograph (original 8X), cross section of a wire nut showing position of spring wire (Type 58).

1. The exposed grains of the latent image	2. The unexposed grains of the latent image
3. The developed silver	4. The undeveloped silver halide
5. The oxidized developer	6. The developer which is not oxidized
7. The neutralized alkali	8. The alkali which is not neutralized
9. The hardened gelatin	10. The unhardened gelatin

Fig. 12-28. Table of "images" present in silver halide emulsion exposed and treated with developer.[2]

Reference 2 continues:

> One direct approach is to form the positive on that second sheet which we are using to confine the viscous liquid when it is being spread. If we can somehow print on this sheet from the negative immediately after the viscous reagent is applied to it, then we are free to try to use any of the images—even including the silver—as an intermediary in forming our positives.

Reference 1, which remains a basic reference on one-step image transfer, includes a comprehensive discussion of possibilities for processes based on the utilization of several of the above images, classified as follows:

A. Exhausted developer processes
B. Oxidized developer processes
C. Soluble silver complex processes
D. Coupler processes.

Exhausted developer processes are defined as those which use the unoxidized developer (6) in Fig. 12-28 to form a positive image in the receiving layer. This class includes the Polacolor and SX-70 dye developer processes.

Oxidized developer processes utilize the oxidized developer (5) directly to form the final positive image, either by bleaching a dye or by forming a white pigment against a dark background.

Soluble silver complex processes transfer images of silver, utilizing images (4), (6) and (8)—that is, the undeveloped silver halide, the unoxidized developer and the alkali not neutralized. This class includes both the initial one-step process and the current black and white processes.

The coupler processes of Class D comprise the coupling developer analogs of Classes A, B and C. Examples of one-step color coupler processes are described in the later section on dye image processes.

Reference 1 includes a comprehensive discussion of the inherent advantages and limitations of processes of each class and describes devices for optimizing each, with attention to their application to both color and black and white systems.

The Camera. The camera for one-step processes yielding direct prints must provide precisely controlled exposures over a long range. Since the range of light intensities which a print can provide is usually less than 100 to 1 and since the range of light intensities (the product of illumination and reflectivity) encountered in most scenes is many times that, the exposure must place the subject accurately within the useful response range of the positive process. The degree of control of exposure which suffices in ordinary negative-positive photography does not suffice in a direct print process, and the techniques used in multi-step processes to compensate for errors in negative exposure are not possible in a one-step process. To avoid the errors which accrue in sequentially reading an exposure meter and setting lens aperture and shutter speed, as well as to avoid the inherent variability of conventional between-the-lens shutters, the earliest one-step camera design simplified exposure control by coupling shutter speed and aperture. A single setting of the Model 95 camera exposure value (EV) scale set the speed of a high precision pendulum shutter and selected one of a series of fixed apertures.[21]

In succeeding one-step camera designs new devices evolved, ranging from automatic galvanometer-controlled shutters[22] and extremely accurate photometers to fully automatic electronically controlled sensor and shutter systems.[23] Figure 12-29 shows in schematic form the controls and shutter of the Model 100 camera, the first camera to control automatically the duration of exposure by measuring and integrating light intensity during exposure. Electronic circuitry performs the integration and actuates the closing of the shutter at the end of the exposure interval. The automatic shutter thus shares with the photographer the burden of retaining tonal gradation in highlights and shadows for that portion of the scene of particular interest to the photographer.

An important mutation in shutter design opened the field of very low cost one-step cameras. The remarkably simple, yet highly accurate, photometer[24] incorporated in the Swinger camera (1965) was the first to use the principle that one can perceive readily only one gestalt at a time in a given area. One of the gestalten is a checkerboard that reverses from black on white to white on black, vanishing at the reversal point, when there is a photometric match between one set of squares. illuminated by an internal light source, and the other set of squares, illuminated by the scene. Superimposed on the checkerboard is a lightly engraved word, "YES." When the checkerboard is visible the "YES," though present, cannot be perceived; when the checkerboard vanishes the "YES" appears vividly. The trigger knob, as it is rotated, closes down the shutter diaphragm in unison with the diaphragm admitting light from the scene to the photometer. The trigger knob is rotated until the "YES" appears and then the trigger knob is depressed to take the picture. About 13.7 million cameras using photometers of this type had been manufactured by the end of 1975.

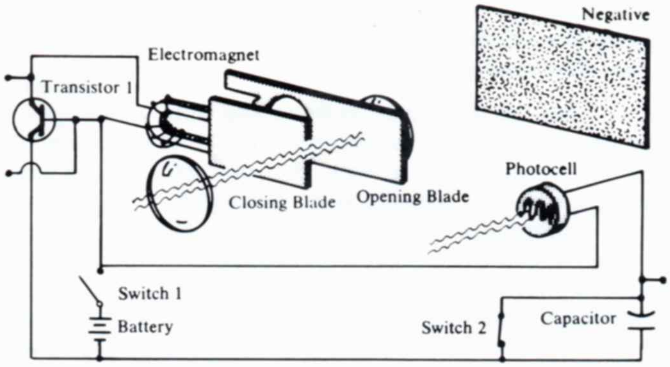
A further special requirement for the one-step camera was, of course, provision for the independent processing of each film unit immediately after exposure. Figure 12-30a, taken from Ref. 1, shows an early schematic plan for a one-step camera equipped with a pair of steel pressure rollers, through which the film was to pass

Cocked Position

Closing blade is out of light path.

Solid side of opening blade blocks light path.

Switch 2 is closed; capacitor is discharged.

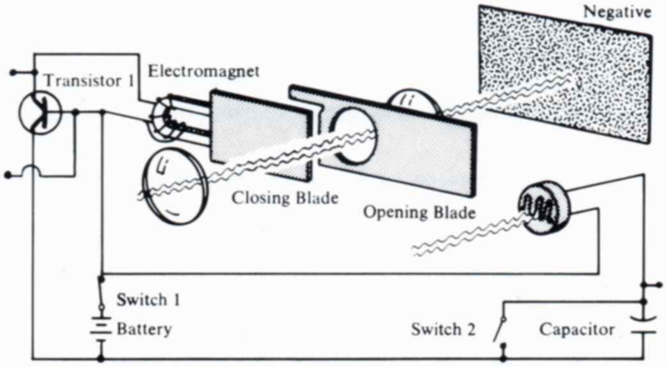


Start of Exposure

Aperture of opening blade moves into light path; exposure begins.

Switch 1 closes; electromagnet holds closing blade in cocked position.

Switch 2 opens; current flowing through photocell charges capacitor.



End of Exposure

When capacitor is charged, spillover current activates transistor 2.

Transistor 1 loses base current and breaks electromagnetic circuit, releasing closing blade.

Closing blade moves into light path.

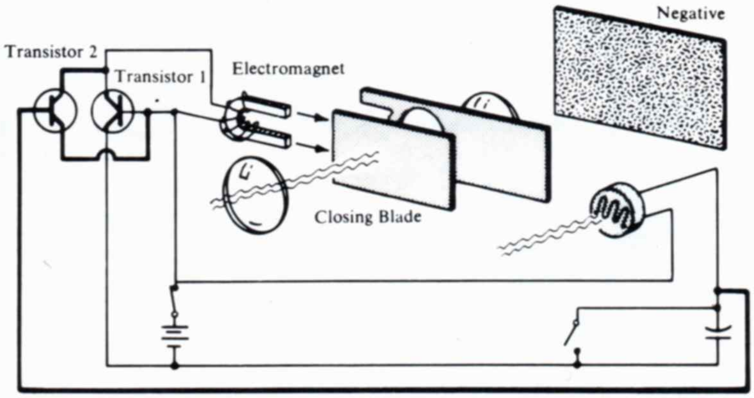


Fig. 12-29. Automatic shutter control system of the Model 100 camera, first camera to control exposure duration by measuring and integrating light during exposure.

after exposure in order to convert the image carried by the exposed grains into a finished picture. The operation of the system was described as follows:

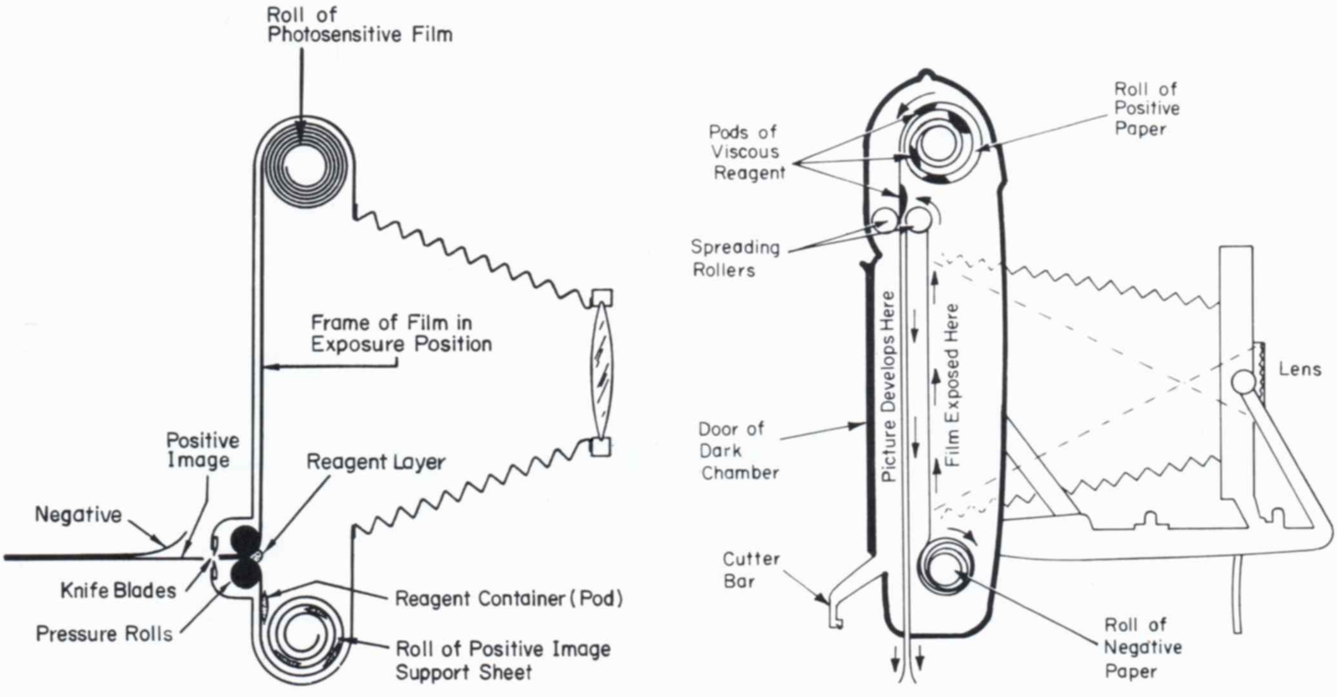
> The camera . . . has the usual lens, bellows and film cartridge for the negative. An additional sheet . . . feeds out of the camera, along with the exposed negative, through a pair of pressure rolls. A reagent, in the form of a minimum amount of liquid, is fed between the two sheets just before they enter the pressure rolls, so that it is spread as an extremely thin layer between the two sheets, temporarily bonding them together. The sheets have outer surfaces opaque to actinic light to protect the negative from being fogged. The thin reagent layer develops the negative and forms the positive on one of the inner surfaces.[1]

Figure 12-21 and Figs. 12-30b through 12-33 illustrate the principal processing formats. The earliest cameras completed the processing inside a dark chamber; later camera models provided for drawing the sandwich of film, pod and receiving sheet between the rollers and out of the camera.* Finally, the SX-70 camera, described in the first section, automatically ejects each picture unit, passing it between the rollers as soon as its exposure is completed. In each case the reagent-spreading system is an integral part of the camera design.

One-Step Processing; The Pod. The important concept of processing in a single "dry" step was fulfilled by a series of interacting measures, which included packaging the liquid reagent in an elongated container or pod[26] as long as the width of the picture, raising the viscosity of the liquid by adding a high molecular weight, film-forming polymer,[27] and distributing the liquid in a viscous state. All of this made possible frame-by-frame processing and the use of fresh reagent for each frame. A vital aspect of the idea of the pod was to attach it to one of the sheet components so that the pod and sheet are transported together; the pod seal ruptures and reagent spreads between two sheets as they pass together through the rollers.

The design of viscous reagents and sealed pods for use in conjunction with a camera having pressure rollers is described as follows in Ref. 2:

> A useful approach is to assume that an amount of liquid that will develop a given area of negative will suffice to form a positive by whatever process we later devise. It is easily shown that a negative can be developed by a very thin layer of strong developer and the experimental results are consistent with the computations for the required amount of developing agent. . . . The amount of developing agent, the



(a) (b)

Fig. 12-30. (a) An early schematic diagram of a camera to produce one-step positive prints (1947);[1] (b) schematic section of Model 95 camera (1948). With the Model 95 and subsequent roll film cameras using "40" and "30" series films, processing is completed inside the camera. A paper leader which extends outside the camera is pulled forward to draw the negative and the positive sheet (to which the pod is affixed) together between the rollers. The pod ruptures, and a thin, uniform layer of the viscous reagent spreads between the two sheets. When the specified period has elapsed, the user opens the latching camera back and peels the positive print away from its negative. After the first picture has been processed, the portions of the two rolls between picture areas serve as leader.

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*Instead of rollers, nonrotating spreaders have been used in some cameras.[25]

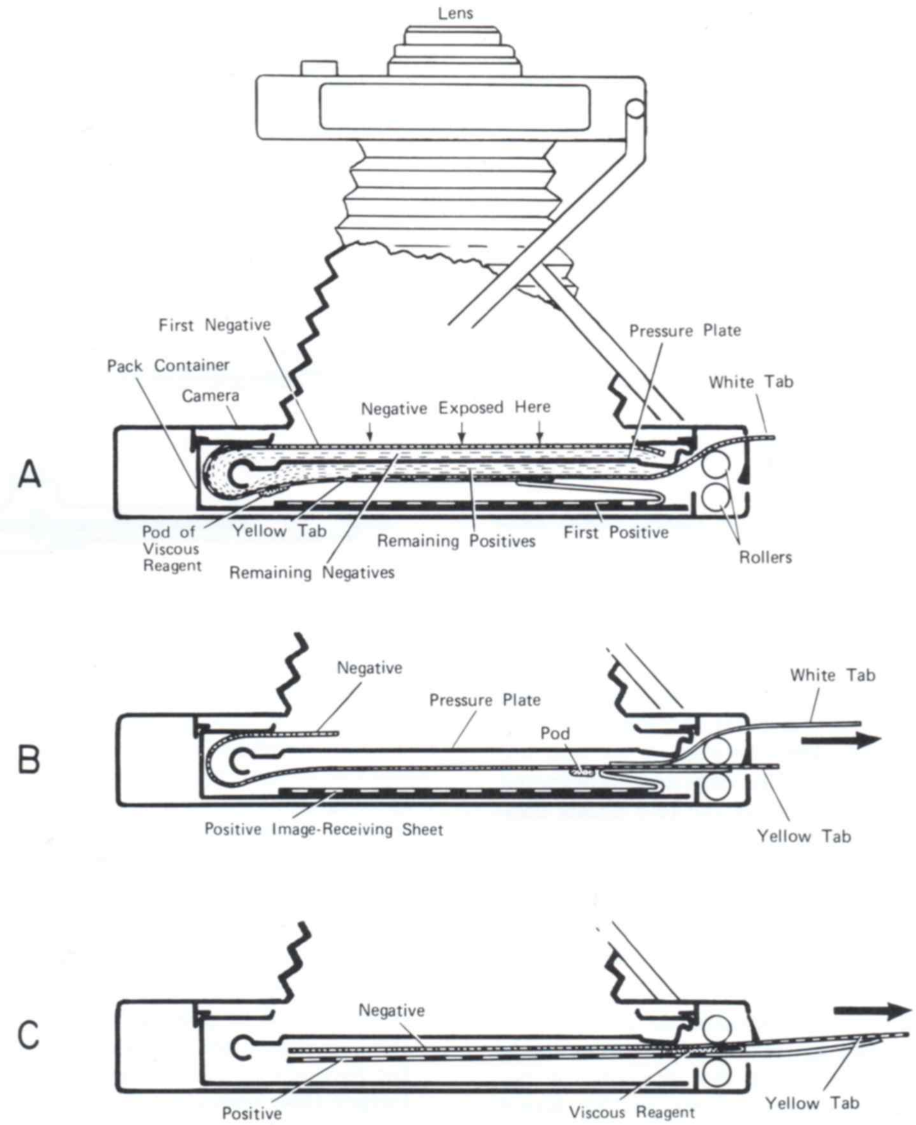

Fig. 12-31. Schematic section of Model 100 camera (1963), illustrating processing of "100" series pack films outside the camera. Both negative and positive sheets have opaque outer surfaces. (A) Pack with each element in the position it occupies at the time of exposure; (B) after exposure a paper tab is pulled to lead the negative into a new position opposite a positive image-receiving sheet; (C) pulling a second paper tab (to which the pod is attached) leads the entire unit between the pressure rollers and out of the camera, rupturing the pod and spreading reagent between the two sheets.

amount of alkali, and the amount of liquid are determined by the requirements of the *single area of negative with which these reagents are associated.* . . . It turns out that when a developer is prepared for use in this way, 0.05 cc per square inch* is adequate to develop a negative, corresponding to a layer a few thousandths of an inch thick. This then is the order of quantity of liquid per unit area which we must confine within our film and which must be released and uniformly distributed by the pressure rolls to perform the processing.

A number of methods were studied in which the liquid was pre-spread at the time of manufacture and simply made available to the negative by the pressure rolls. In one of those methods, the developer is contained in minute frangible cells which are ruptured either by pressure, or by tension produced by bending around a roll with a small radius. These frangible cells reside in one stratum of the film and their liquid contents, after they are broken, migrate to other strata.

An entirely different method was actually selected for initial use. . . . In this method the developer is not pre-spread but resides in flat, folded, hermetically sealed pods, one for each frame. In addition to the negative, a second sheet of film or paper is used, and the pods lie between the negative and this second sheet. The pressure transmitted from the rollers through the sheets

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*0.008 ml/cm^2.

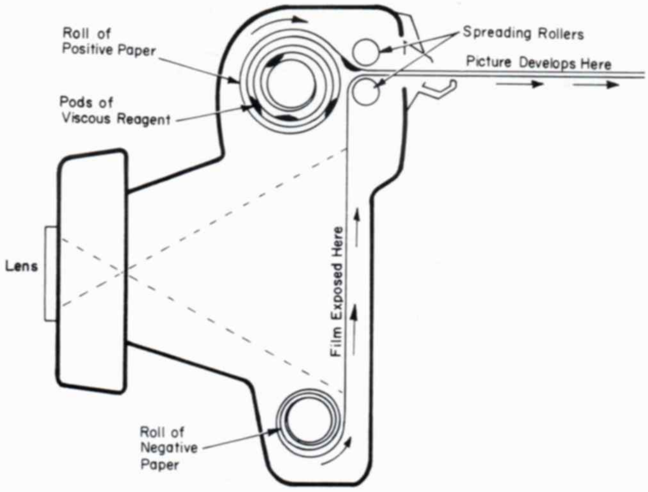

Fig. 12-32. Schematic section of Swinger camera (1965), illustrating processing of "20" series roll film outside the camera. Both sheets have opaque outer surfaces. The user draws the "sandwich" between the rollers and out of the camera in a single motion. Compare with Fig. 12-30a.

> to the liquid content of the pod builds up the hydraulic pressure within the pod to burst the leading edge* along its whole length. The contents of the pod are discharged parallel to its leading edge and transported over the area of the negative as the two sheets continue through the camera rollers. The liquid is immediately imbibed by the adjacent inner surfaces and proceeds to carry out the photographic processes. The *outer* surfaces of the sheets, even when porous material is used, remain dry because of the small amount of liquid required.
>
> One would wonder if it is possible to confine and control a liquid spread in this way. . . . It is made entirely feasible by increasing the viscosity of the liquid. By adding thickening agents to the liquid content of the pod its viscosity is increased to the order of 30,000 centipoises. At this viscosity, the liquid can be spread as a layer of controlled thickness between the two sheets. This viscous layer, about 0.003 inch thick, serves many purposes: it is a reservoir of known volume for metering reagent and solvent to the sheets; it provides a temporary adhesive to hold the two surfaces in flat face-to-face relationship; it can be made to collapse in thickness rapidly so that, when desired, an image-forming interaction between the surfaces may operate over a short working distance; if a plastic is used as the thickening agent, it can be left as a lacquer on one of the sheets; the image can, if desired, be formed in this plastic layer or the image can be formed under it. The thickening agent can serve as a protective colloid during the period of image formation, and it can serve as a sink for holding salts in solid solution on the finished picture or for removing them from the picture when the other sheet is stripped away. . . . We are enabled to use a metered amount of fresh reagent for each reaction and to provide these strata (the surfaces of the two sheets and the layer of viscous liquid) as loci for reagents which can be brought together at will to initiate their interaction.

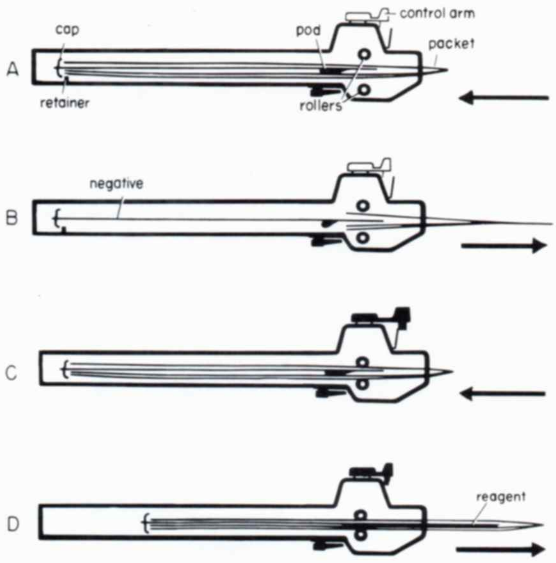

Fig. 12-33. Film Holder for 4 × 5 in. packets, used in professional press and view cameras and in the Polaroid MP-3 and MP-4 industrial cameras. Processing rollers are contained within the holder, and each film packet is a light-tight unit. When the packet is inserted into the holder (A), a spring-loaded retainer engages a cap on the end of the packet, so that the outer envelope may be partially withdrawn and the film exposed (B). The photographer then reinserts the envelope (C) and sets the control arm to processing position, which brings the rollers into position against the packet and retracts the retainer. He then pulls the entire packet through the rollers and out of the holder (D). The packet is stripped apart after the appropriate processing time.

The sealed pod of viscous reagent thus conceived has been an essential part of each of the one-step products. Despite serious efforts to develop alternatives the very reliable and highly versatile pod remains a preferred reagent carrier for dry film assemblies.** A typical pod structure is illustrated in Fig. 12-34.

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*In some systems the rollers are transported over a stationary assembly of negative, positive and pod; early work of this type led to defining the leading edge of the pod as the edge through which the viscous reagent was ejected.

**The pod lining must be inert to concentrated alkali and reducing agents. Even though it is a solid film, the lining must not be a solvent for reagent components. The lining must not contain plasticizers which could hydrolyze or be emitted into the reagent. The pod must be sealed in such a way that it is opaque to water vapor and to oxygen over a period of years, yet in such a way that the seal will rupture over its whole length simultaneously; if one portion ruptured first, the liquid would all go through the orifice created by the local rupture. The seal must not become brittle at low temperature or tacky at high temperature; it must be strong enough not to rupture when film units are rolled or stacked, yet not so strong that the pod will pass through the rollers without opening at all.

One of the earliest pod designs comprises a layer of paper on which is a layer of lead foil and then a layer of polyvinyl butyral. The edge is striped on one side with ethyl cellulose. At the short edge the polyvinyl butyral provides a thermoplastic seal; along the long edge it provides the peelable bond with ethyl cellulose. Both the polyvinyl butyral and the ethyl cellulose are stable to alkali. Most modern pods are lined with polyvinyl chloride.

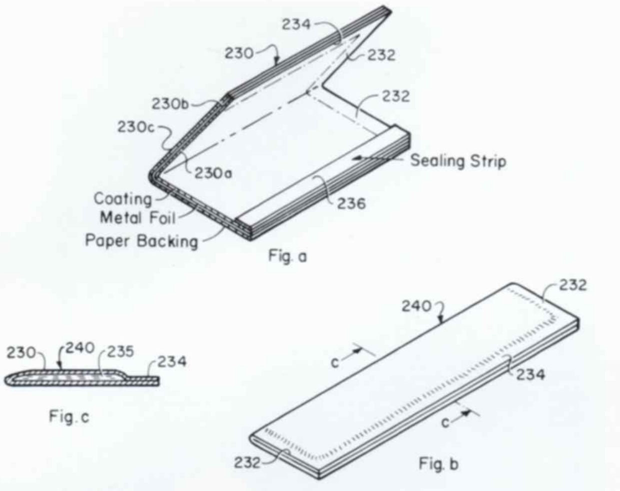

Fig. 12-34. A patent illustration showing a typical pod structure.[26]

Pods opened a new domain of developer activity and film speed. It was found possible to make the reagent* highly alkaline and much more strongly reducing than conventional developers. Reagents too reactive to be stable in open tank processing are readily preserved by confinement in pods; each pod is a container for fresh reagent in the amount required to process a single picture, and each portion is used only once. The pod and sheet system makes possible exclusion of oxygen from the time the reagent is sealed in the pod until the final image is complete.

The reagent within the pod may include any or all of the chemicals used for developing a negative image and depositing a positive image quickly and virtually simultaneously, each in the proper location. The pod reagent may include such addenda as antifoggants and development accelerators. It is particularly useful to incorporate and isolate within a pod components which would be unstable or incompatible in a sheet structure, just as it is useful to incorporate in the sheet components which would be unstable in the liquid developer. If a silver image is to be formed in the layer of reagent, as is the case in the transparency version of black and white films, the reagent may contain nucleating materials as well. In the SX-70 color film structure the pod contains the white pigment and indicator dyes, as described earlier.

Polymers suitable as thickeners for pod reagents include the alkali-soluble salts of carboxymethyl cellulose, hydroxyethyl cellulose and carboxymethyl hydroxyethyl cellulose. These polymers are often used in the highest molecular weight—i.e., highest viscosity—grades. The quantity used is a function of the desired viscosity and the viscosity of the polymer, the higher viscosity grades permitting the use of smaller concentrations of polymer, frequently with attendant increases in transfer rates of image-forming components.

Early Image Transfer Experiments

Dye Images. In devising processes for the one-step camera, Land drew upon his background in the development of image transfer processes for making Vectograph prints; (1938).** To test the principle of controlling imagewise transfer of dye by an intermediate image in tanned gelatin, a paper-based emulsion was exposed in a camera, developed in a tanning developer and immediately passed through a wringer in contact with a layer of blotting paper saturated with a solution of an acid dye. When the two layers were separated after a minute, dye had transferred through the differentially hardened emulsion layer to form a positive image in dye in the paper base; the emulsion layer bearing the negative image in silver was subsequently stripped away.*** One of the earliest such pictures, made in 1944, is reproduced in Fig. 12-35†.

Silver Image. The next experiments examined the transfer of silver from a developing negative to a hardened gelatin layer. The gelatin layer was prehardened with formaldehyde and presoaked in a solution containing both developer and fixer. When the presoaked gelatin layer was passed through the wringer in contact with an exposed negative, a brown, continuous tone positive image of finely divided silver was deposited in the gelatin within one to two minutes. Figure 12-35b is reproduced from a picture made in 1944 by this procedure.‡

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*The term "reagent" is used broadly to describe the total liquid processing composition rather than an individual reactive chemical component.

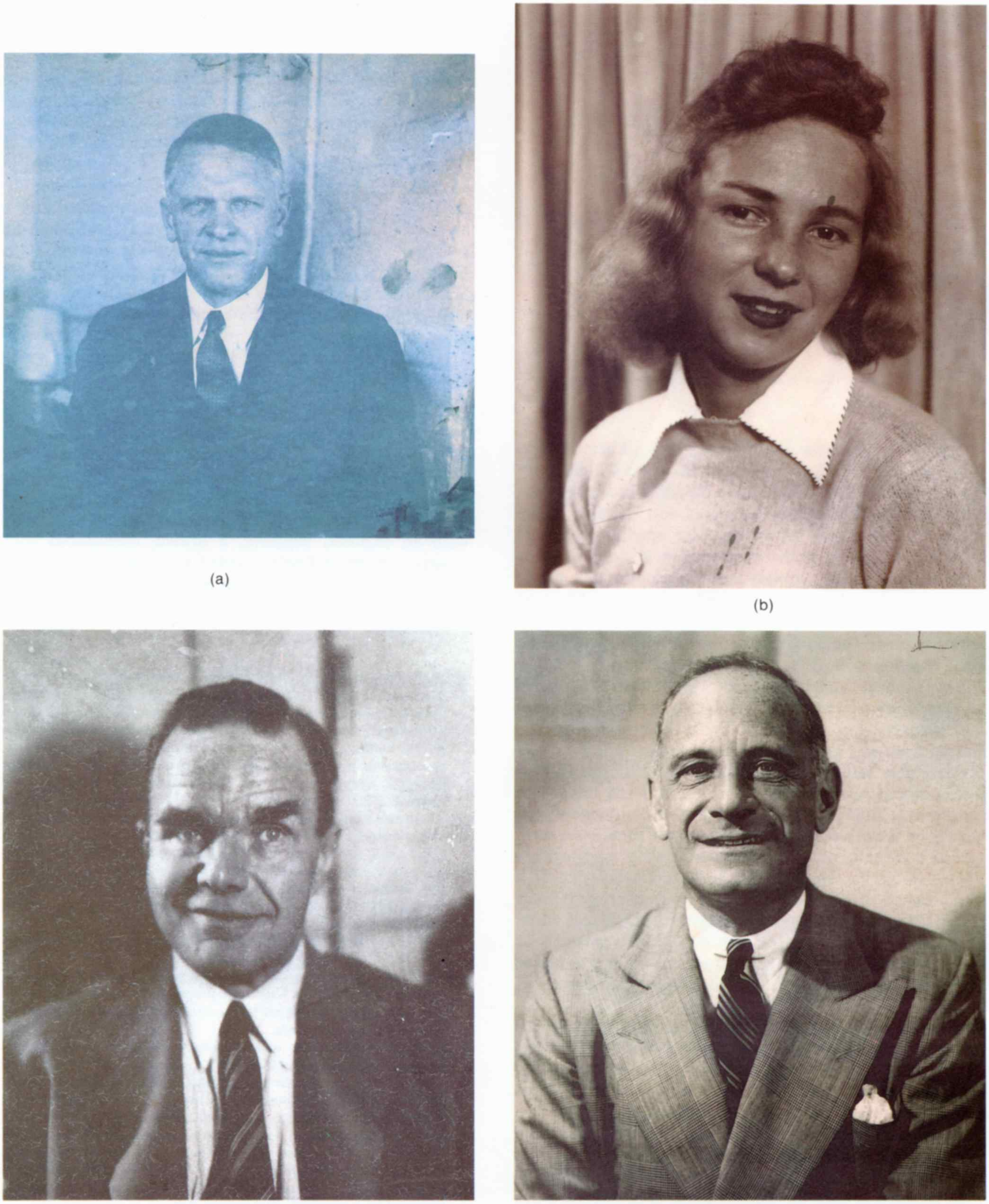
**Polaroid Vectograph prints comprise oppositely polarized image pairs—i.e., images in terms of vectorial inequality which, when viewed through oppositely oriented polarizing filters, yield three-dimensional images.[28] In the Vectograph process, paired positive gelatin matrices, prepared by conventional tanning development, are soaked in a solution of a dichroic dye or iodine, and the imbibed images in dye or stain transferred to layers of polyvinyl alcohol oriented at 90° to one another. Transfer is accomplished by passing a "sandwich" of the wet reliefs with the Vectograph sheet between them through a wringer. Vectograph transfer images have also been made using an original negative directly as a printing matrix. In this process, the developed negative is dipped into an iodine solution, iodine is abstracted imagewise by reaction with the silver of the negative image, and the unreacted iodine is transferred to form a positive image in the vectograph sheet.

***A process based on similar principles is described by Schering-Kahlbaum A. G. in a 1931 patent.[29]

†All of the reproductions of early photographs included in this chapter were made in 1976. They were prepared directly from the original photographs, which are still in excellent condition in the Polaroid Corporation archives.

‡Other processes which utilize undeveloped silver halide by dissolving, transferring and reducing it in a second layer were derived independently by Weyde at Agfa and by Rott at Gevaert.[30] Rott applied for a British patent in 1939 and obtained a U.S. patent in 1944 on processes based on the transfer of soluble silver complex from a negative after it had undergone substantial development.[31] Transargo, a document copy material using this princple, was marketed by Gevaert in Belgium during 1940 and 1941; its positive sheet contained hypo and silver sulfide nuclei, and transfer was followed by a selenium after-toning step.

Weyde's early work resulted in Norwegian patents issued in 1942 and 1944 to I. G. Farbenindustrie for processes using organic sulfur compounds, sulfides or colloidal silver with gelatin receiving layers.[32] Agfa's first silver transfer product, Veriflex, was produced during the war years. This material was described as a two-layer reflex copy film with silver chloride coated over a layer containing silver



(a)

(b)

(c)

(d)

Fig. 12-35. Examples of early image transfer processes: (a) Dye image transferred through negative layer hardened imagewise (1944); (b) Silver image deposited in gelatin (1944); (c) Silver image deposited in α-cellulose blotting paper (1944); (d) Silver image formed in crosslinked polymeric reagent, using as receiving sheet baryta paper impregnated with lead acetate (1945).

Image and Process Specifications. Having devised working transfer processes for images both in silver and in dye, Land addressed his next experiments toward outwardly dry, one-step processes yielding silver images of neutral tone and dye images suitable for three-color subtractive photography. Whether in black and white or in color, continuous tone photographs would require images of constant hue at all densities. For use in a one-step process, a film of suitable speed and its accompanying reagent would need to be self-contained and stable in storage. The system would need to complete the single processing step rapidly and to produce pictures which would be stable without washing. New materials and new methods were required to provide one-step cameras and processes which could effectively meet these specifications.

The following pages describe and illustrate the principles involved in fulfilling the requirements of one-step camera processes. The section on *Silver Image Processes* will be devoted to the development of the initial one-step film system and of subsequent black and white products; the section on *Dye Image Processes* will cover the concurrent development of one-step color systems.

SILVER IMAGE PROCESSES

Image Formation; Color and Structure

One of the first problems to which Land directed his attention in the development of silver processes was the influence of the method of formation of the image deposit upon its structure and upon its spectral characteristics.

Images in Thick Gelatin Layers. The brown color of the transfer images formed in a gelatin receiving layer, as in Fig. 12-35b, was attributed to a distribution of small particles spread far apart.* Recent microscopy of the 1944 images in gelatin shows those deposits to comprise fine particles 10 to 30 nm in diameter formed into aggregates of a wide range of sizes, from 20 to 300 nm in diameter. The aggregates are distributed throughout a 10 to 12 μm depth, and neighboring aggregates are 1 to 6 diameters apart, as shown in Fig. 12-36a.

The gelatin matrix could evidently influence both nucleation and growth of the image aggregates. The action of gelatin as a highly protective colloid is essential in the emulsion to prevent premature decomposition of the soluble silver complex within that layer; a gelatin receiving layer would similarly inhibit formation of the positive silver aggregates. In the same gelatin layer, however, impurities could concomitantly serve as sites for nucleation—the greater the number of sites, the smaller the aggregates thus formed. The gelatin layers first used as receiving layers had been prepared by fixing and washing sheet films, so that residues might have served as nuclei.**

Formation of Compact Images. The image problem at this stage was twofold: to grow particles in an image-receiving layer directly from solution and to grow them as nearly as possible to a uniform and appropriate size. A thin image layer would provide a close-packed deposit, so that the particles could interact electromagnetically, approaching the conductive properties of a metallic layer. Ideally, the layer would be expanded just enough to be a black absorber rather than a mirror.

To demonstrate that precipitation would occur spontaneously without the protection of the gelatin and to facilitate the growth of a compact layer of large particles, Land used a nonprotective receiving layer of α-cellulose blotting paper, which is readily penetrable but insoluble. Once the silver complex left the emulsion layer it would be free to precipitate within the surface of the α-cellulose paper. When an exposed negative was pressed against a sheet of the α-cellulose blotting paper which had been prewet in a solution containing developer and hypo, a positive image outstanding for its

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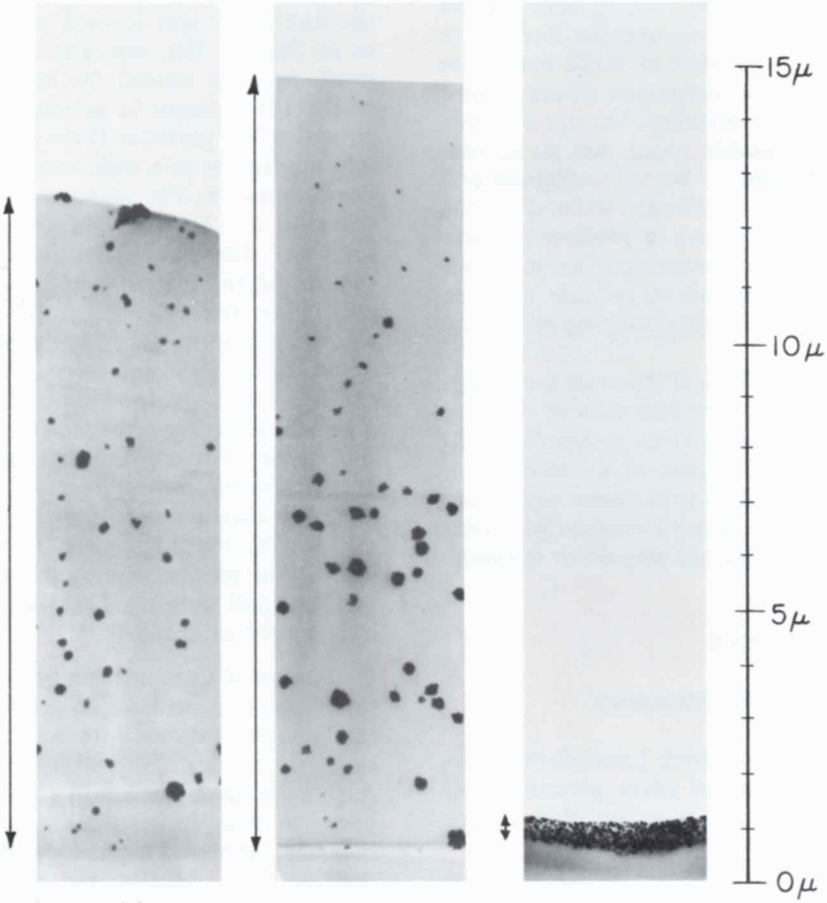
nuclei and zinc oxide; after a positive image had formed in the nucleating layer, the negative was washed off with warm water and the zinc oxide dissolved by acetic acid to leave a positive transparency.[33]

Further work by both Rott and Weyde led to successful two-sheet document copy processes, both introduced subsequent to the first Polaroid one-step camera process. Agfa's Copyrapid was first marketed in 1949 and Gevaert's Gevacopy in 1950. In Copyrapid and Gevacopy processing, an exposed low speed, high contrast negative sheet was introduced into a liquid activator bath simultaneously with a positive sheet having a gelatin receiving layer containing nuclei; the two sheets were thereafter brought into contact between pressure rollers and then stripped apart, yielding a transferred positive image. Unlike the Polaroid process, the copy processes were based on emulsions of low speed. They produced image deposits having line rather than continuous tone images, and the image hue was thus not critical. Document copy materials and processes are discussed in detail in Chapter 11 and in Ref. 30.

Earlier workers had described different image transfer phenomena in silver halide systems. The transfer of soluble silver salt images from unexposed areas of a developing silver chloride emulsion into a gelatin layer containing the developer had been reported by Liesegang in 1898.[34] Other early observations included those of Lefevre, who in 1857 transferred silver from a daguerreotype soaked in hypo to a layer of gelatin;[35] of Colson, who reported in 1898 the transfer of a negative image in terms of oxidized developer,[36] of Stenger and Herz, whose 1922 German patent claimed processes for the transfer of positive images in terms of unoxidized developer;[37] and of Stevens and Norrish, whose 1938 paper described transfer of an image from a silver halide negative to a gelatin-coated plate after wetting both with developer and subsequent physical development of the transferred image.[38]

*The 1911 data of Chapman Jones[39] had indicated the dependence of color upon size of silver particles suspended in gelatin; Jones had enlarged fine silver particles by coating them with mercury and had observed transmission colors from yellow to gray over a calculated range of diameters from 100 to 190 nm. He reported that he found no correlation between particle separation and color for particles between 1 and 10 diameters apart.

**To examine the question of nucleation by impurities, images formed in gelatin layers of this type were recently compared with images formed in coatings of refined gelatin deionized to minimize impurities. The images in the deionized gelatin comprised larger aggregates, as if indeed there were fewer points of initiation. In this purified gelatin the aggregates ranged up to 400 nm in diameter, and the image tone was bluish. Figure 12-36b shows the structure of the image in deionized gelatin, and Fig. 12-37 compares transmission spectra of images in the two gelatins.



(a) (b) (c)

Fig. 12-36. Comparison of images deposited in impure and purified gelatin and in the pores of α-cellulose paper. Length of arrow beside each cross section shows thickness of region populated by silver particles: (a) is from a picture such as the one reproduced in Fig. 12-35(b), with the deposit in a thick layer of gelatin prepared by fixing and washing a sheet of commercial film; (b) is from a deposit in a thick layer of highly purified gelatin; and (c) is from an image formed in α-cellulose blotting paper; (c) is shown at higher magnification in Fig. 12-38. Spectra of (a) and (b) are shown in Fig. 12-37, and the spectrum of (c) in Fig. 12-39.

neutral tone was deposited in the near surface of the paper. A picture made in 1944 in this manner is reproduced in Fig. 12-35c.

Figures 12-36c and 12-38 are electron micrographs showing in cross section an image deposit recently prepared by the above procedure. The image comprises single crystalline particles rather than aggregates, the individual crystals being closely packed in a layer only 400 nm thick, less than 1/25 the thickness of the earlier image deposits in gelatin, to form a near-continuum of silver at maximum density. The single crystals in the α-cellulose paper measure 15 to 150 nm in diameter, somewhat smaller than the aggregates in gelatin. Figure 12-39 shows the strikingly uniform spectral reflectance of this compact positive image.

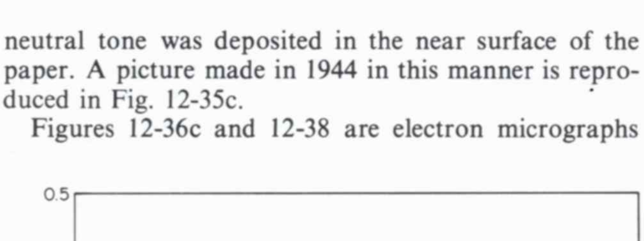


Fig. 12-37. Transmission spectra of the images in thick gelatin layers shown in Figs. 12-36(a) and (b).

In succeeding experiments spectrally neutral silver images were deposited in regenerated cellulose layers prepared by the alkaline hydrolysis of cellulose acetate sheet. The image deposits comprised aggregates ranging up to 300 nm in diameter, with most of the silver in the larger aggregates in a 2–2.5 nm stratum close to the sheet surface.

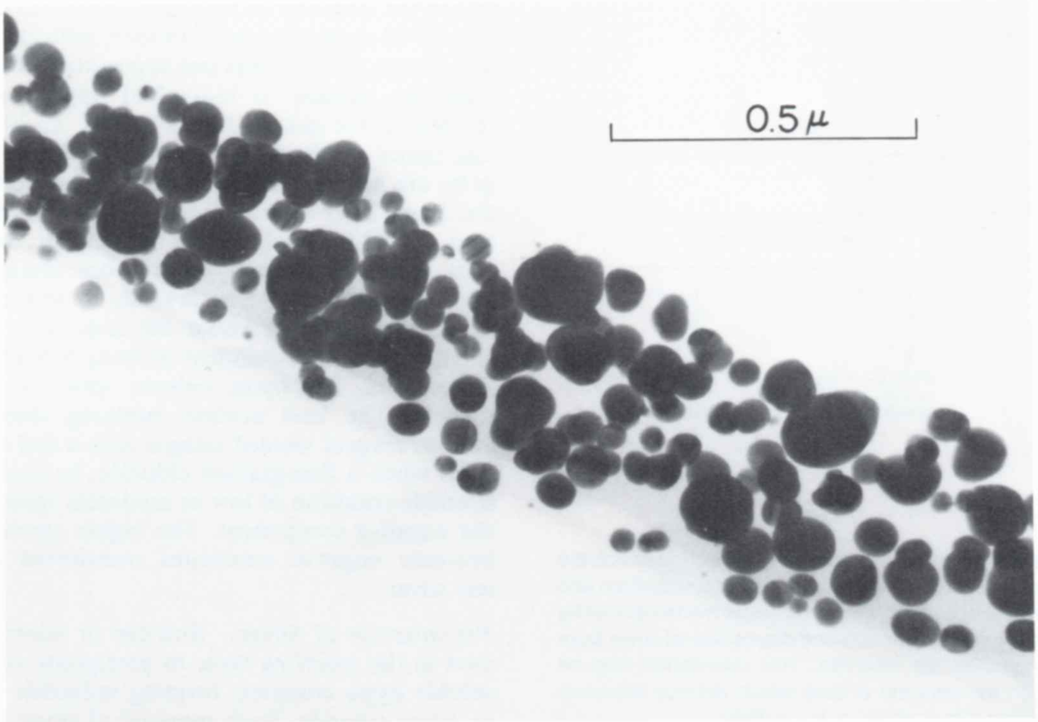


Fig. 12-38. Cross section of neutral image in α-cellulose blotting paper. Note that the deposit of crystals is compact but not solid, an ideal condition for blackness. Reflectance spectrum is shown in Fig. 12-39.

In both the pure α-cellulose blotting paper receiving layer and the regenerated cellulose receiving layer the deposition process, characterized by Land as "concentration and condensation," depends on the local concentration of soluble silver complex becoming sufficiently high to initiate precipitation. As no nucleating materials are added, the soluble silver is presumably nucleated—much as raindrops are—by sites accidentally present in low concentration in the capillaries of the blotting paper or within the regenerated cellulose layer. These are powerful examples of receiving systems not seeded with nuclei and not inhibited by a protective colloid.

Processing with Viscous Reagent. The compact silver layers in α-cellulose blotting paper and in regenerated cellulose had been identified as structures suitable for neutral, continuous tone images, but the procedures which were used to form them did not lead directly to a one-step camera process. The next step toward the camera process was to produce such an image using a viscous reagent which could be sealed in pods and incorporated in the self-contained film units described earlier.

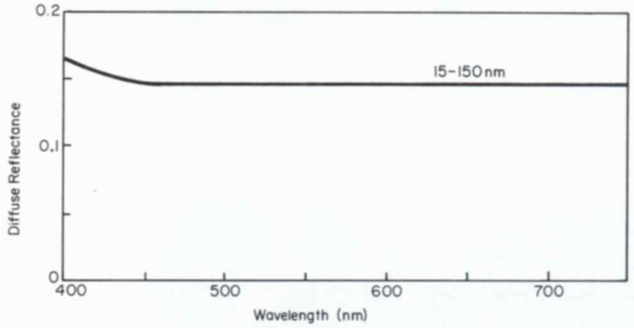


Fig. 12-39. Spectral reflectance of image deposit in α-cellulose blotting paper, shown in cross section in Figs. 12-36(c) and 12-38.

An important consequence of using a reagent made viscous with a polymeric thickener is that the polymer retards precipitation of silver from the soluble complex. In order to achieve reduction and precipitation in an image-receiving layer, it is necessary to overcome this retardation.

Approaches proposed by Land to induce the release of silver from its hypo complex in the presence of a retarding polymer include: (a) precipitation of thiosulfate ion,[40] (b) precipitation of a hypo-insoluble, readily reducible silver salt,[41] and (c) nucleation by a colloidal heavy or noble metal.[42] These reactions could be used alone or in combination. Figure 12-40 outlines reactions of types (a) and (b), and processes based on these principles are discussed below.

Precipitation of Thiosulfate. To remove thiosulfate ion, a soluble salt of a metal which forms an insoluble thiosulfate could be added to an image-receiving sheet. Reaction with the soluble silver complex would precipitate the metal thiosulfate salt and free silver ion, which is readily reducible.

A process of this type[40] used as the receiving sheet baryta-coated paper which had been impregnated with lead acetate and dried. When the lead-treated receiving sheet and an exposed negative were passed together

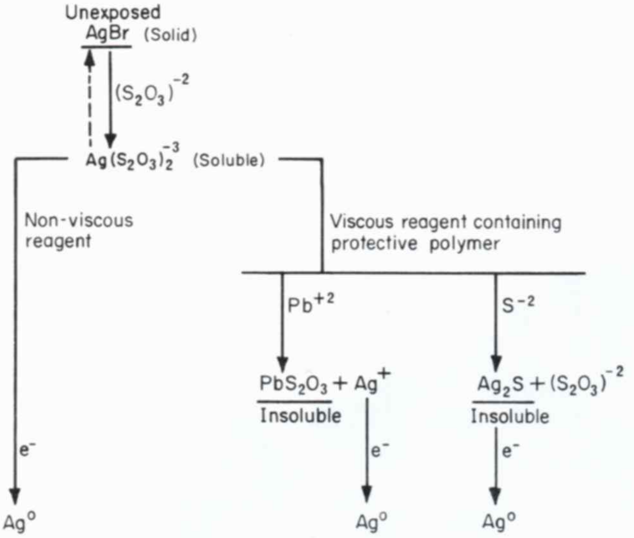


Fig. 12-40. Schematic outline of transfer and reduction of soluble silver complex images. With a nonviscous reagent, reduction and deposition of silver proceed rapidly. In reagents made viscous by the addition of a polymer, reduction and deposition of silver from the thiosulfate complex are retarded. This retardation may be overcome through the addition of ions which destroy the complex by precipitating either silver or thiosulfate.

between pressure rollers, spreading between them a viscous reagent containing developer and hypo, an image of neutral tone and excellent pictorial quality resulted. This process is another example of "concentration and condensation" deposition, as no nucleating materials are added.

Figure 12-35d is a recent reproduction of a print made in 1945 with the lead acetate receiving sheet. Figure 12-41 shows the structure of an image deposit of this type, and Fig. 12-42 shows its nearly uniform reflectance spectrum. The image silver comprises aggregates 20 to 300 nm in diameter, similar in individual appearance to those formed in the gelatin layers of Fig. 12-30. Unlike the aggregates in the thick layers of gelatin, these aggregates are arranged compactly. They are confined within the 2 μm layer of crosslinked polymer formed by reaction of lead ion with the viscous reagent; the aggregates thus comprise a nearly continuous image deposit at high densities. The fine crystals in this deposit form dense aggregates of about the same size as the large, single crystals in α-cellulose blotting paper, as described above, and, like them, behave optically as black absorbers. The lead acetate receiving sheet used with viscous reagent yielded images with a full range of densities when a fine-grained chloride, bromide or chlorobromide emulsion of low or moderate speed was used as the negative component. The higher speed silver iodobromide negative emulsions transferred considerably less silver.

Precipitation of Silver. Sulfides or selenides could be used in the receiving layer to precipitate silver from the soluble hypo complex, forming reducible silver sulfide or silver selenide. Such removal of silver ion from the thiosulfate complex frees thiosulfate for further extraction of silver ion from the remaining silver halide.

When soluble sulfides were added to the receiving system, deposition of positive silver from the complex was indeed increased, but a new gamut of problems, described as follows in Ref. 2, resulted:

(1) Sulphide (sic) ions in solution provide so many points of initiation that an enormous number of

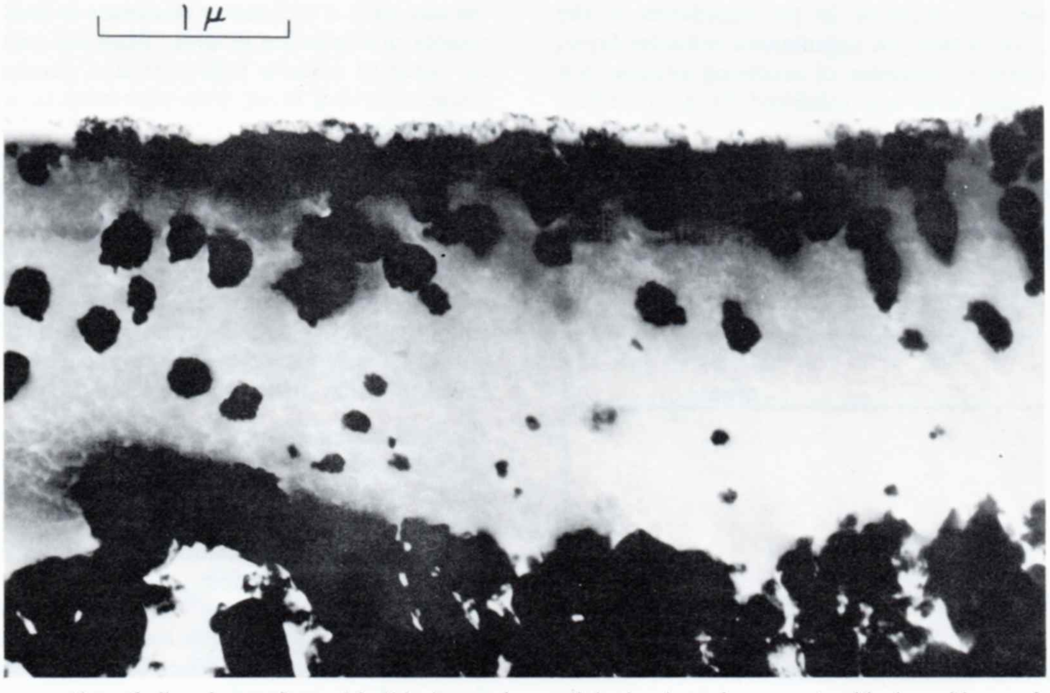


Fig. 12-41. Cross section of silver image formed in thin layer of crosslinked polymeric reagent, with deposition assisted by soluble lead ions in positive sheet. The large particles seen in the lower region of the section are barium sulfate pigment in the baryta coating.

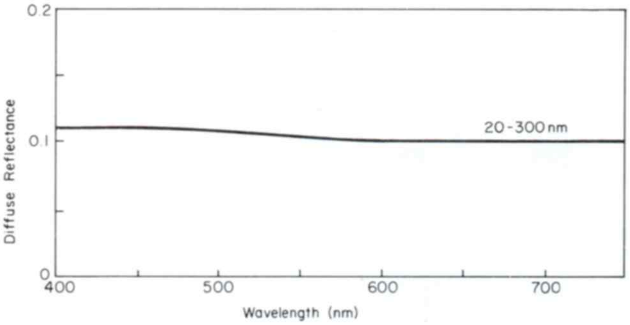


Fig. 12-42. Reflectance spectrum of the silver image of Fig. 12-41. The image comprises aggregates 20–300 nm in diameter.

grains start growing. If these become large the whole picture will be too dense. If they remain small, the picture will be bright yellow (you will recall that the colour of silver colloids depends on the particular size).

(2) There is a tendency for the grains in the shadows, opposite the unexposed portions of the negative, where much silver is available, to grow larger than the grains in the medium tones, where the available silver concentration is low, producing an unpleasant combination of blue shadows and yellow highlights.

(3) Some of the sulphide ions migrate into the negative, dropping the concentration in the positive and fogging the negative.

Thus, having determined how to extract silver ions from the appropriate part of the negative, and how to reduce them to silver atoms, we are still confronted with the problem of how to build these atoms into arrays of the correct diameter for absorbing visible light.

Greater control of the size and number of image deposit sites was achieved by incorporating in the receiving layer a small amount of a finely divided crystalline metal sulfide of low solubility.[41] Sulfide ions would remain localized until complex silver ions from the negative reached them and could thus initiate precipitation of small clusters of silver sulfide particles. The clusters would serve as loci for the deposition of silver in masses appreciably larger than those obtained with the uniformly distributed soluble sulfides.

Silica-based Metal Sulfides. A significant advance in the control of image deposition was the precipitation of the insoluble metal sulfide in a colloidal suspension of very finely divided silica.[43a] The silica, being insoluble and nonswelling, limited the volume within the layer available for precipitation of the sulfide as well as for deposition of silver. Sulfides precipitated in this matrix readily formed fine aggregates or galaxies,[43b] comprising a positively controlled population of active sites.

The sulfide ions were essentially bound in place until they reacted with the soluble silver complex to form silver sulfide. As an additional measure to avoid the release of soluble sulfide ions upon reduction of silver sulfide, an excess of soluble metal ions capable of forming sulfides more soluble than silver sulfide, but still not appreciably soluble in the developer, was included in the receiving sheet.[44] Sulfide ion freed at its original site could thus be at once reprecipitated *in situ* and the diameter of the cluster maintained. The silver image deposits produced in this system were of well-controlled size and distribution and brown or brown-black throughout their entire density range.

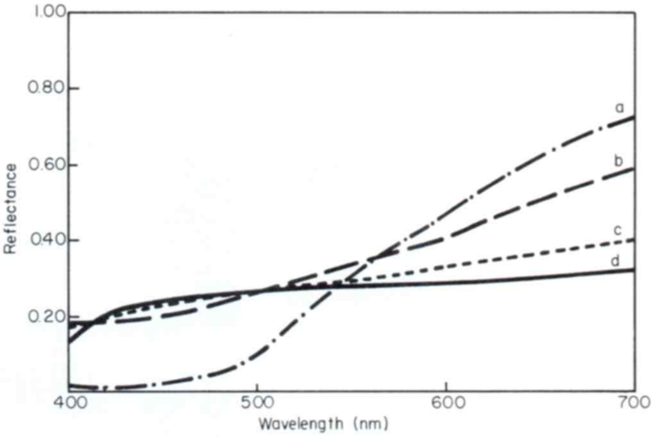


Fig. 12-43. Reflectance spectra of images transferred by viscous reagent to silica-sulfide receiving sheets, comparing the images formed when the receiving layer contains (a) soluble sulfides, (b) uniformly distributed fine crystals of a metal sulfide of low solubility, and (c) and (d) *galaxies* or clusters of very small crystals of a metal sulfide precipitated in a colloidal suspension of silica.

At this point, sulfides had been used to produce image colors from yellow to brown to nearly neutral, as the sulfides were added (a) in solution, (b) as fine crystals uniformly distributed and (c) as galaxies of microcrystals formed in the presence of silica. Figure 12-43, taken from Ref. 1, shows reflectance spectra of such a series of images. It is evident that image color was predetermined by the nature of the sulfide used and that the preferred near-neutral sepia image could best be formed when metal sulfides were precipitated in silica.

The siliceous metal sulfide receiving layer was a fundamental component of the sepia film system first put into production, and newer silica-based receiving layers continue to have a vital role in contemporary black and white systems.[45]

The Sepia Process. The sepia one-step process, publicly demonstrated in 1947,* produced pictures outstanding in pictorial quality at exposure levels equivalent to ASA

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*The demonstration used an 8 x 10 in. view camera equipped with motorized processing rollers and a dark chamber (Fig. 12-44). The film assembly for each picture comprised a silver halide emulsion, a positive image-receiving sheet and, affixed to the positive sheet, a sealed pod filled with viscous reagent. Processing involved simply passing this assembly through the motorized rollers into the dark chamber. The roller pressure ruptured the pod, releasing and spreading the processing reagent between the two sheets, which formed negative and positive images on their respective surfaces. Pictures were taken, and each photograph was displayed 1 min after exposure, its one-step process having thus taken place automatically inside the camera. Figure 12-45 shows a picture of this type being stripped apart after processing through demonstration rollers outside the camera.

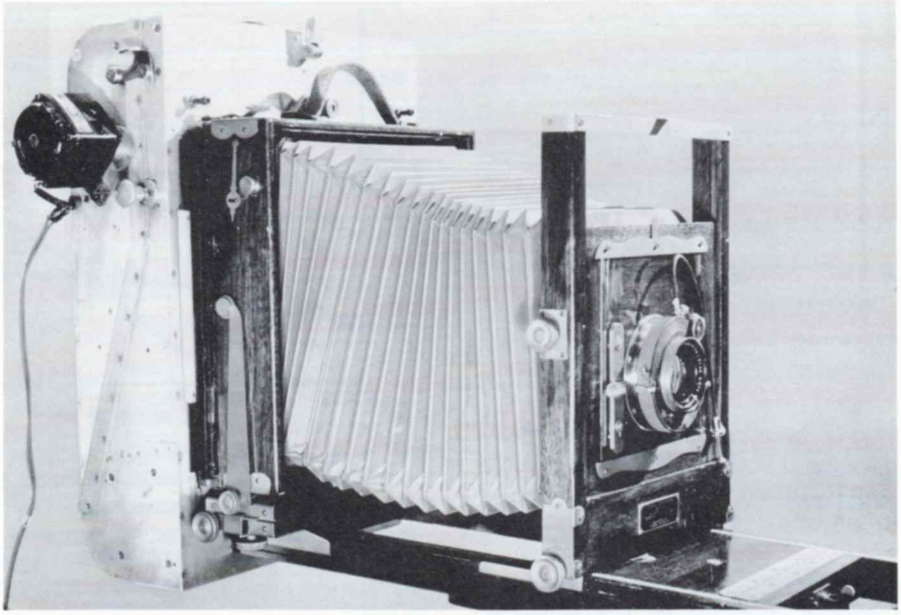


Fig. 12-44. 8 × 10 in. view camera with motorized processing rollers and dark chamber, used in the first public demonstration of one-step photography, February 1947.

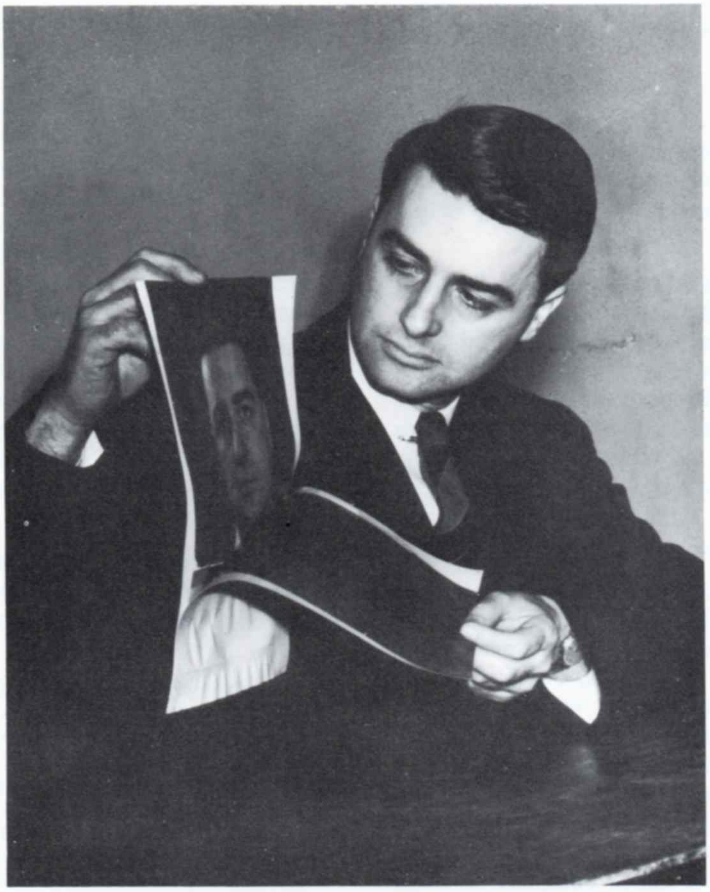


Fig. 12-45. Separation of 8 × 10 in. negative and positive sheets after processing in camera of Fig. 12-44, photographed during February 1947 demonstration by Land.

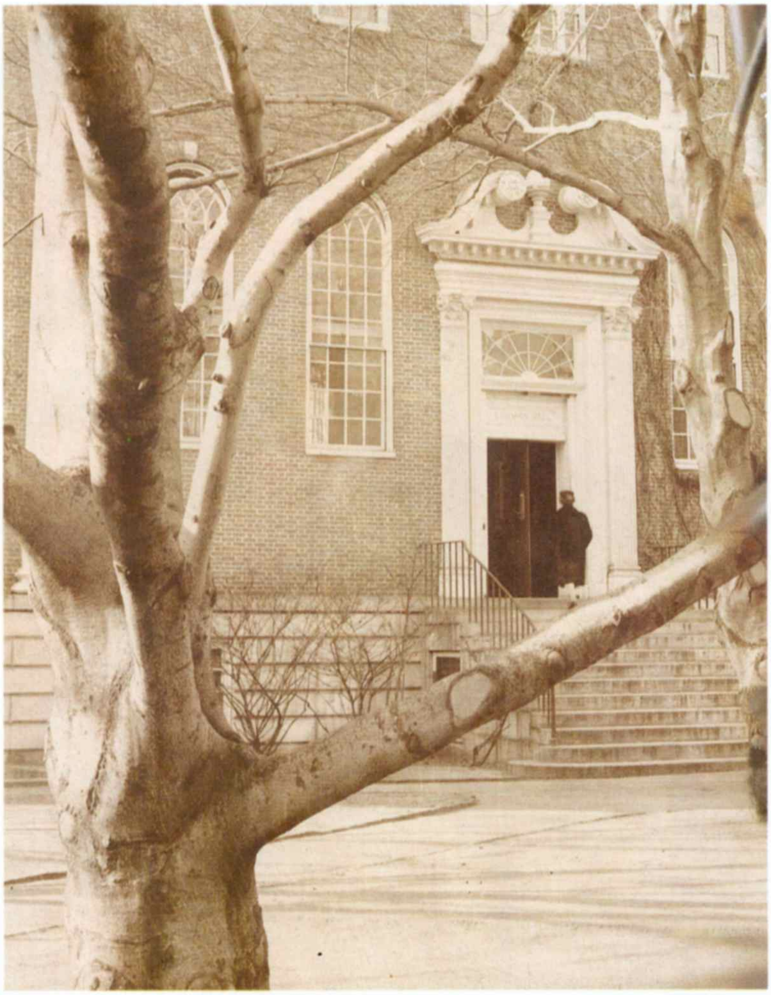


Fig. 12-46. A 1976 reproduction of the 1946 sepia one-step photograph used as an illustration in the first paper on one-step photography.[1] This picture was the first published one-step photograph. The picture, which had no post-treatment and was kept in an ordinary office file, appears unchanged after 30 years.

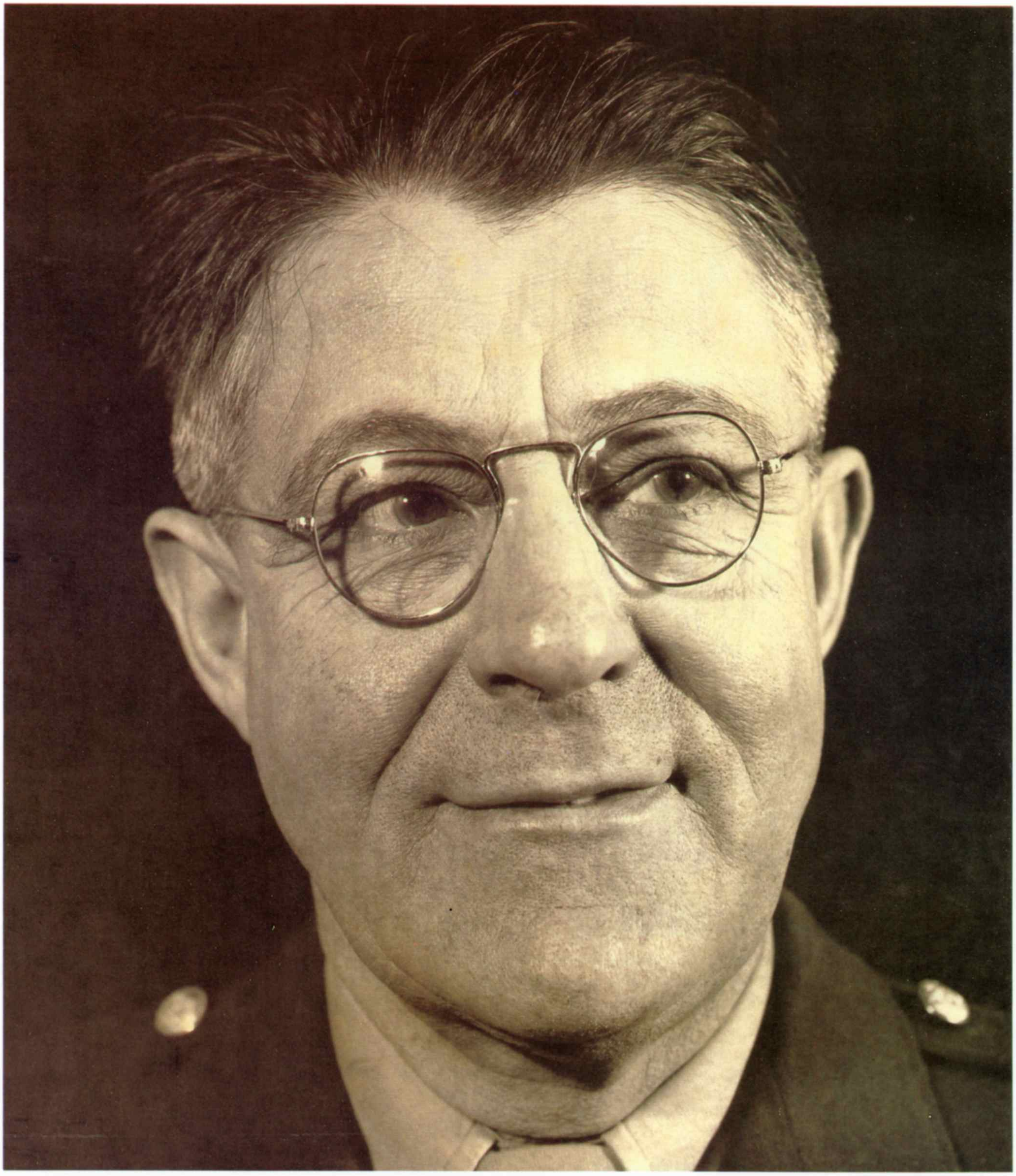


Fig. 12-47a. General George Goddard (1947). Photographed and processed in the camera shown in Fig. 12-44.

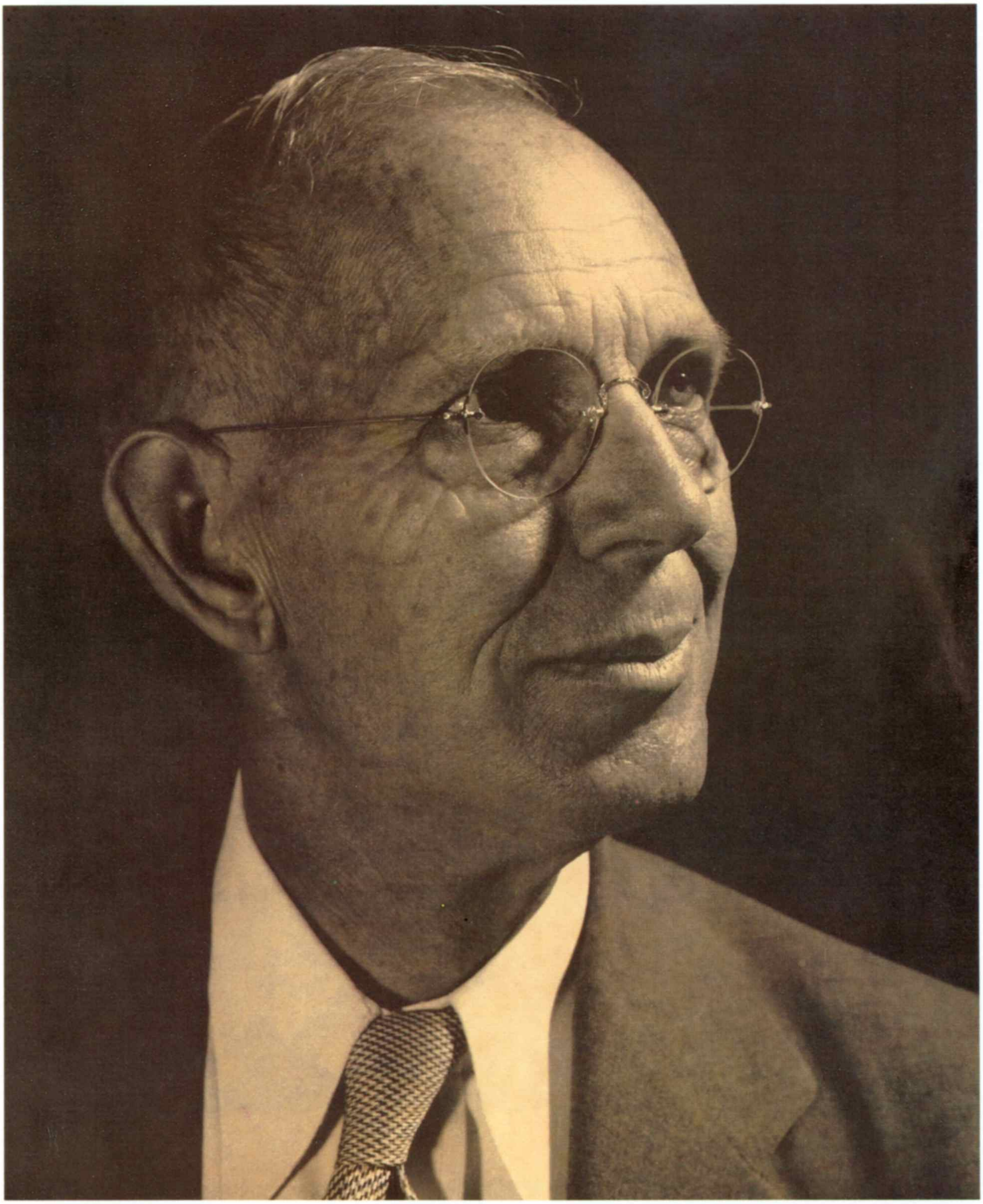


Fig. 12-47b. Professor Clarence Kennedy (1947). Photographed and processed in the camera shown in Fig. 12-44.

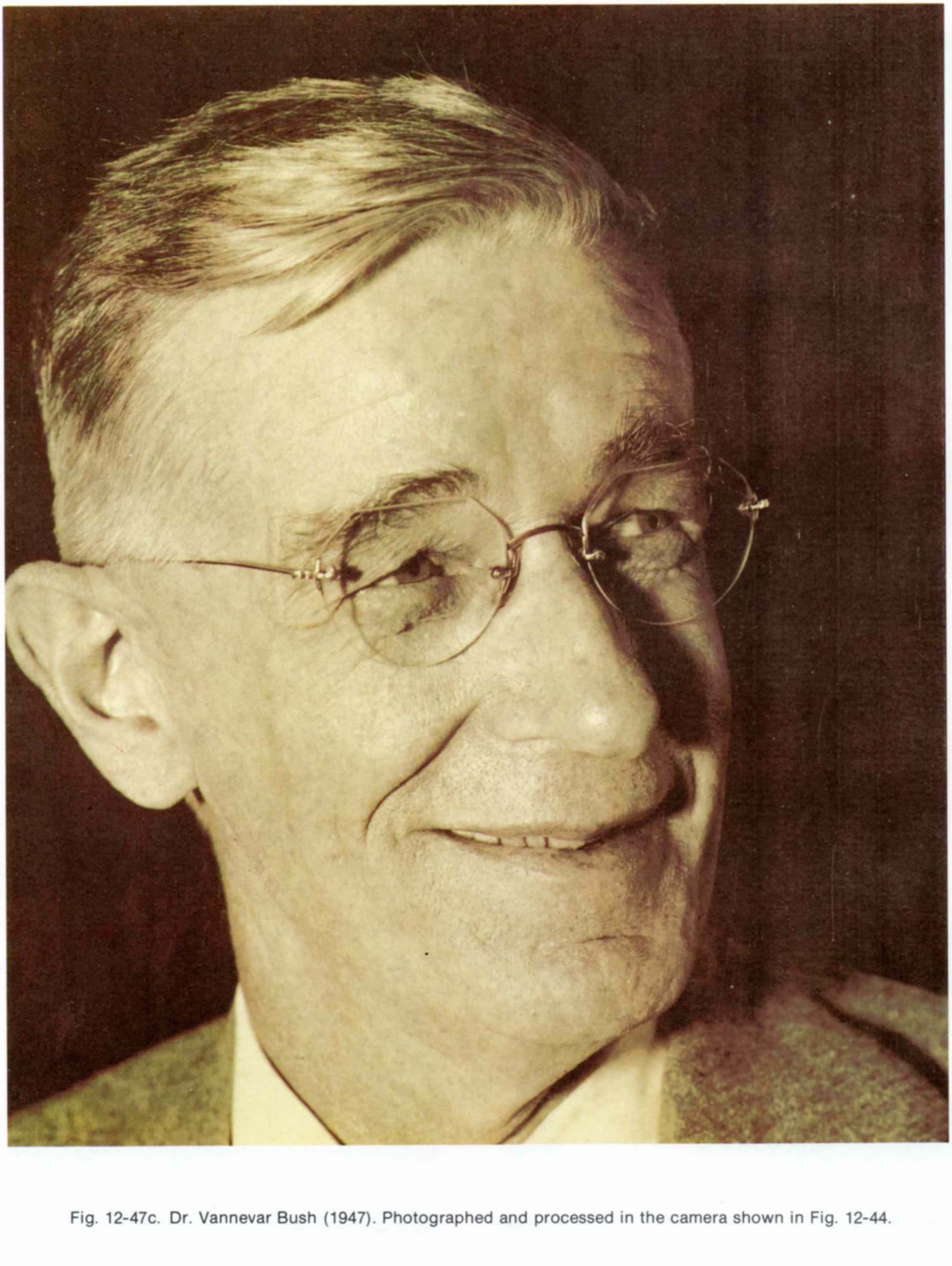


Fig. 12-47c. Dr. Vannevar Bush (1947). Photographed and processed in the camera shown in Fig. 12-44.

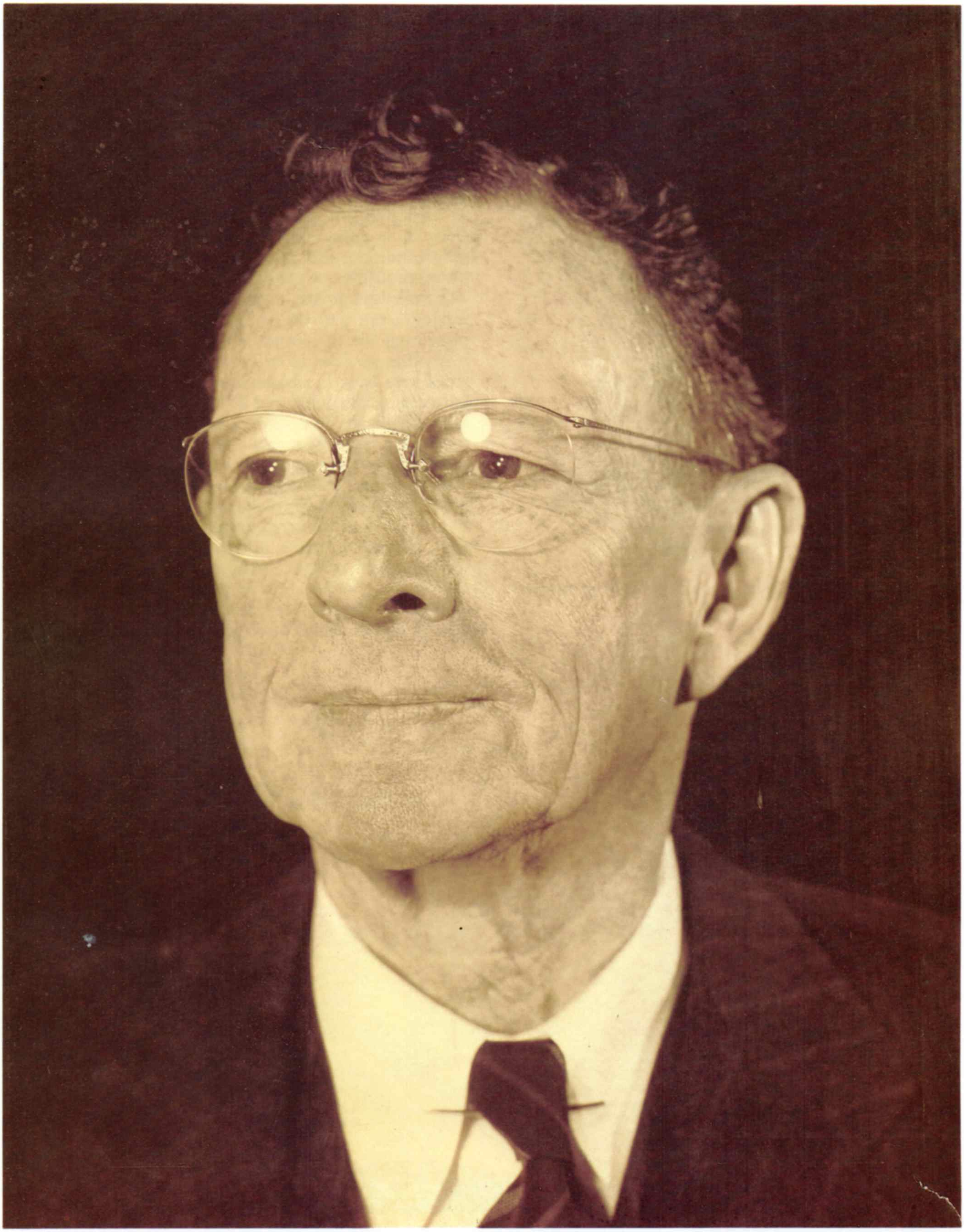


Fig. 12-47d. Dr. William David Coolidge (1947). Photographed and processed in the camera shown in Fig. 12-44.

speed 100. These untreated and uncoated images are remarkably stable, as evidenced by Figs. 12-46 and 47, which are 1976 reproductions of prints made and exhibited in 1946 and 1947. Type 40, the sepia roll-film product, was introduced along with the first one-step camera, the Model 95, in late 1948. (Fig. 12-48).

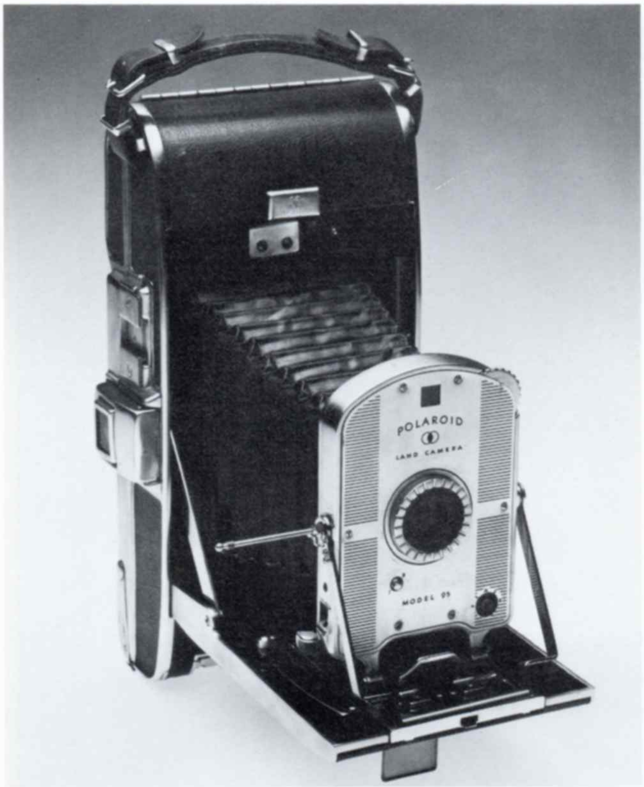


Fig. 12-48. The Model 95, first of the Polaroid Land cameras (1948).

Black and White Processes. The transition from sepia to black and white reflection prints was accomplished by Land and Morse between 1948 and 1950, when Type 41 film was introduced. They precipitated metal sulfides in a silica hydrosol and coated the resulting suspension in a thin layer over baryta paper bearing a waterproof layer of polyvinyl butyral. Image deposition was restricted to the interstices of the silica-based receiving layer, and the image silver formed aggregates measuring 100 to 160 nm in diameter, each comprising many fine particles 10 to 30 nm in diameter. The aggregates were large in comparison with the Type 40 image particles, which measured 25 to 125 nm. The electron micrographs of Figs. 12-49 and 50 show the fine structure of the respective sepia and black and white images, and Fig. 12-51 compares their reflectance spectra.

Subsequent silica-metallic sulfide receiving layers have formed still larger image aggregates. Figures 12-52a and b are electron micrographs of image deposits of high and intermediate optical densities in a current receiving layer of this class (Type 107), showing in cross section the configuration of image silver aggregates in their silica matrix. Figure 12-53a shows a maximum density area as viewed through the layer, and Fig. 12-53b

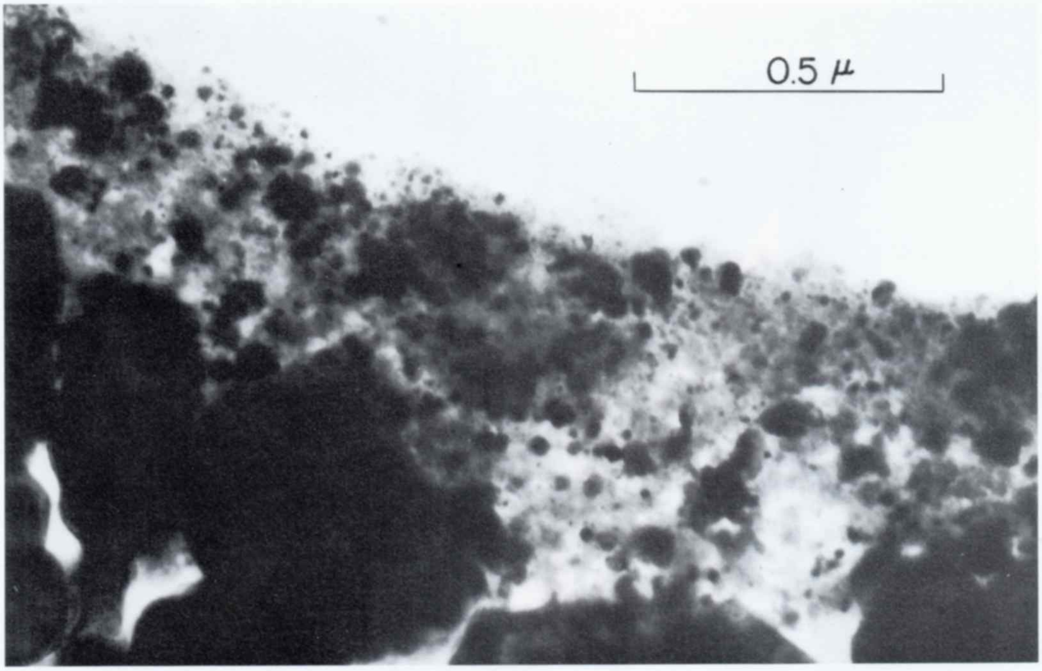


Fig. 12-49. Cross section of image layer of Type 40 sepia print. As in Fig. 12-41, the large particles in the lower portion of the section are barium sulfate pigment in the baryta coating; above the baryta is the deposit of silver in silica.

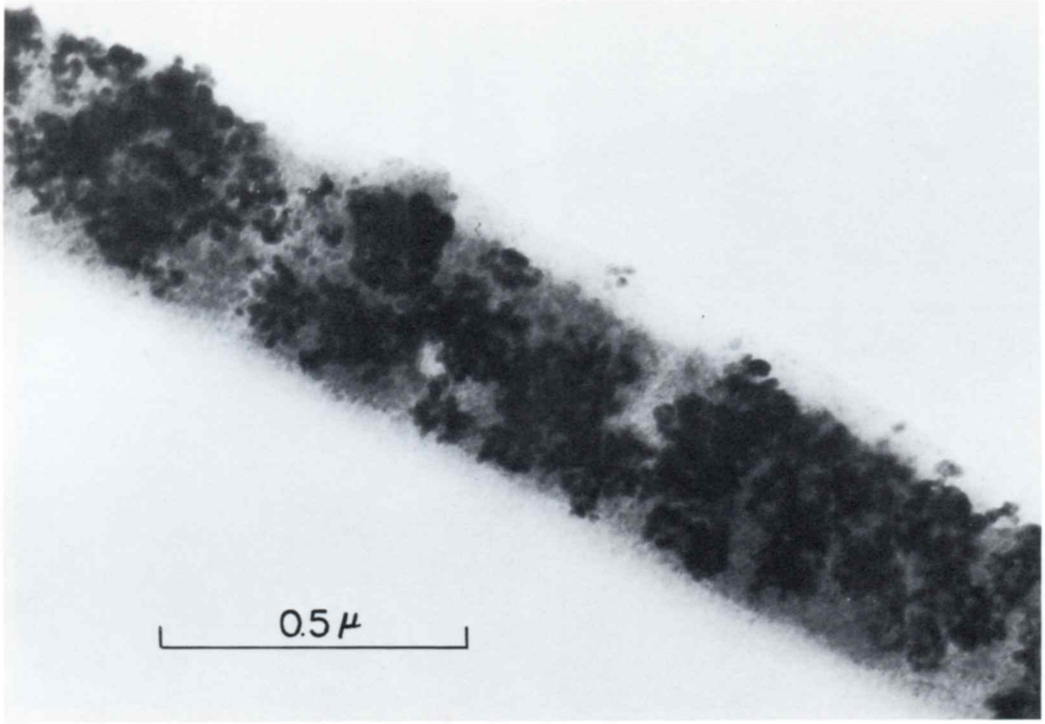


Fig. 12-50. Cross section of Type 41 image, showing silver aggregates restricted to thin layer of silica. Type 41 was the first Polaroid black and white film (1950).

shows a flake of silver aggregates separated from the silica matrix, demonstrating the continuous nature of a high density image deposit; Fig. 12-54 shows a single aggregate at higher magnification. The aggregates average 150 to 300 nm in diameter; each comprises about 40 closely associated particles 15 to 20 nm in diameter. Figure 12-55 shows the consistent neutral reflectance spectra of a Type 107 image over its full density range.

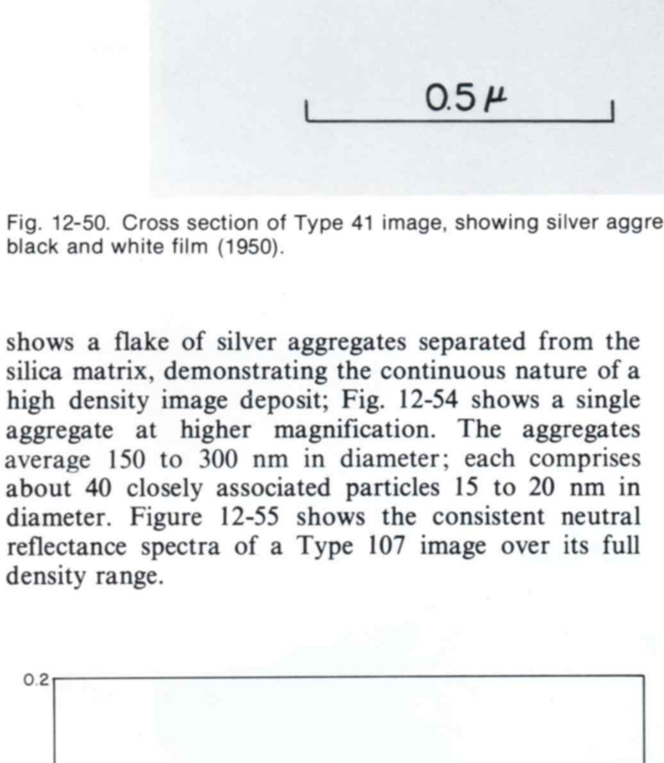


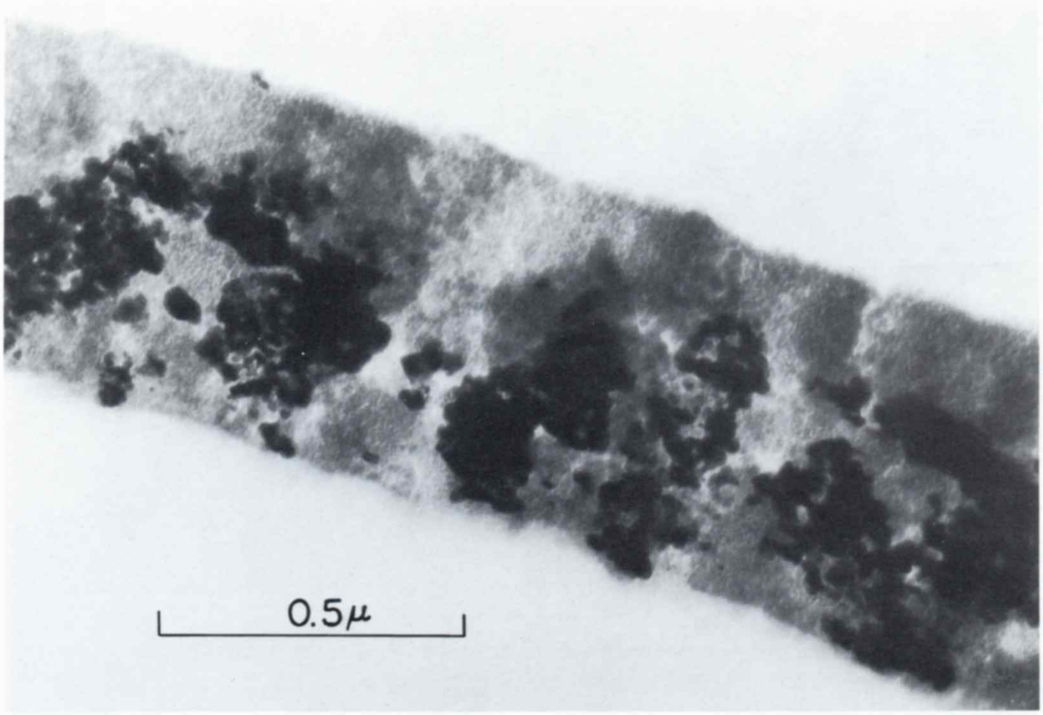
Fig. 12-51. Reflectance spectra of Type 40 sepia image (dotted line) and Type 41 black image (solid line). Numbers printed over curves indicate range of image aggregate diameters.

Nucleating Sites in Regenerated Cellulose. As noted earlier, regenerated cellulose was one of the first materials found suitable as a matrix for neutral silver image deposition. Using nonviscous reagents, nucleation and growth of silver took place readily in the absence of added nuclei.

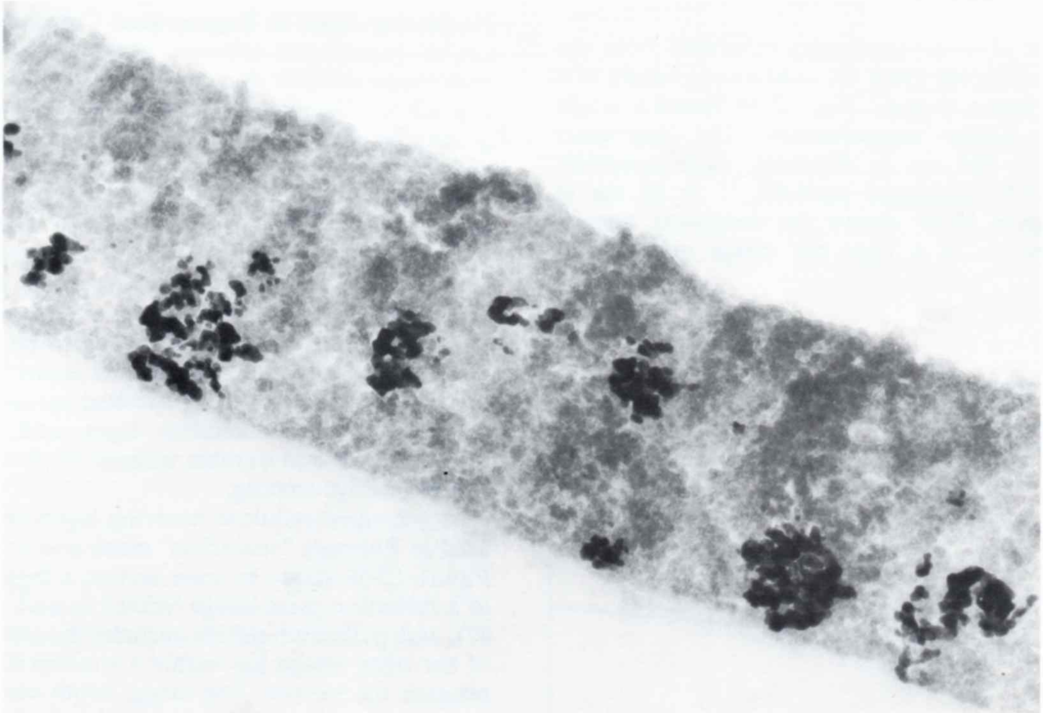
Nuclei found suitable for incorporation into regenerated cellulose layers for use with viscous reagent systems include colloidal metals and colloidal metal sulfides and selenides. Image-receiving layers of regenerated cellulose having nuclei of well-controlled size and distribution are obtained by hydrolyzing a cellulose acetate layer containing the desired nuclei.[46] With sheets of this type image silver is deposited beneath the surface of the regenerated cellulose layer, and the resulting print is glossy and durable without the later application of a protective coating.

Regenerated cellulose receiving layers of this type are used in Polaroid "coaterless" black and white systems.* Figure 12-56 shows in cross section a high density area of a reflection print image formed in such a layer (Type 87), with palladium sulfide particles the active sites. Most of the silver image lies within a stratum 0.04 to 0.4 μm beneath the surface. The image depth corresponds approximately with the depth to which the layer had been hydrolyzed prior to image formation. The image silver includes both large aggregates of fine crystals and large single crystals, with deposits of each type ranging up to 200 nm in diameter.

*"Coaterless" systems are those yielding positive prints which are stable without coating or other aftertreatment. Further discussion is included in the section "Stabilization of Transferred Images," p. 318.



(a)



(b)

Fig. 12-52. Type 107 image silver, (a) cross section of a maximum density area (1.65) and (b) cross section of a density 1.14 area. The aggregates are embedded in silica; the dark regions are silver, the light gray silica.

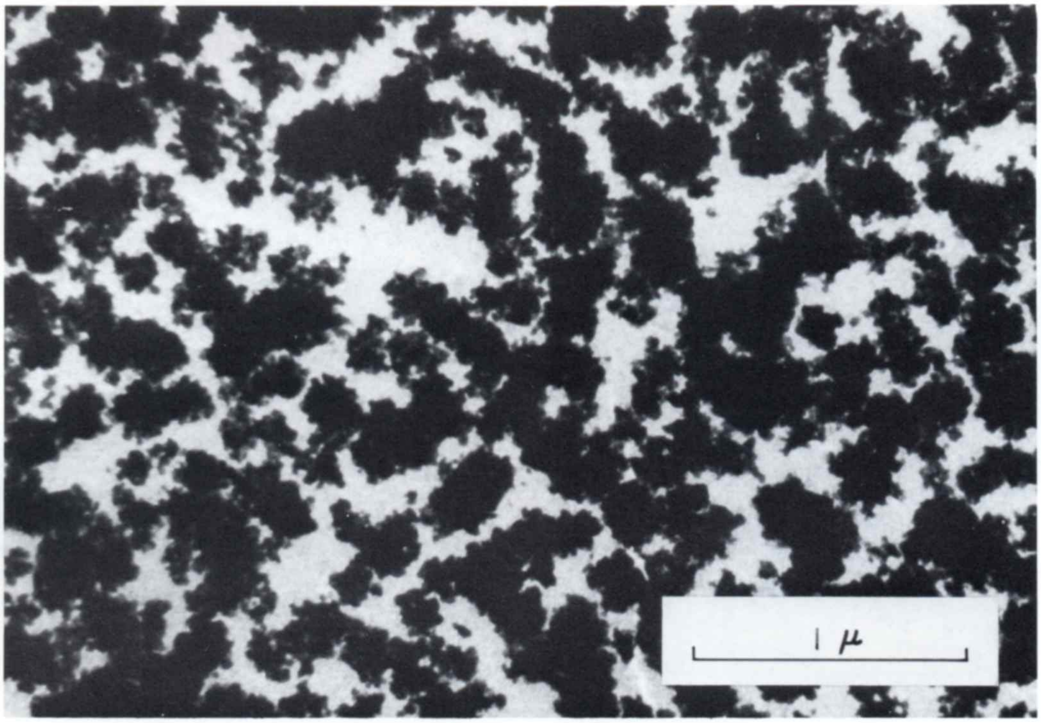


Fig. 12-53a. Type 107 image silver in maximum density area, as viewed through the layer. The magnification here is somewhat lower than in the cross section of Figs. 12-52(a) and (b) to provide a more extensive field of view.

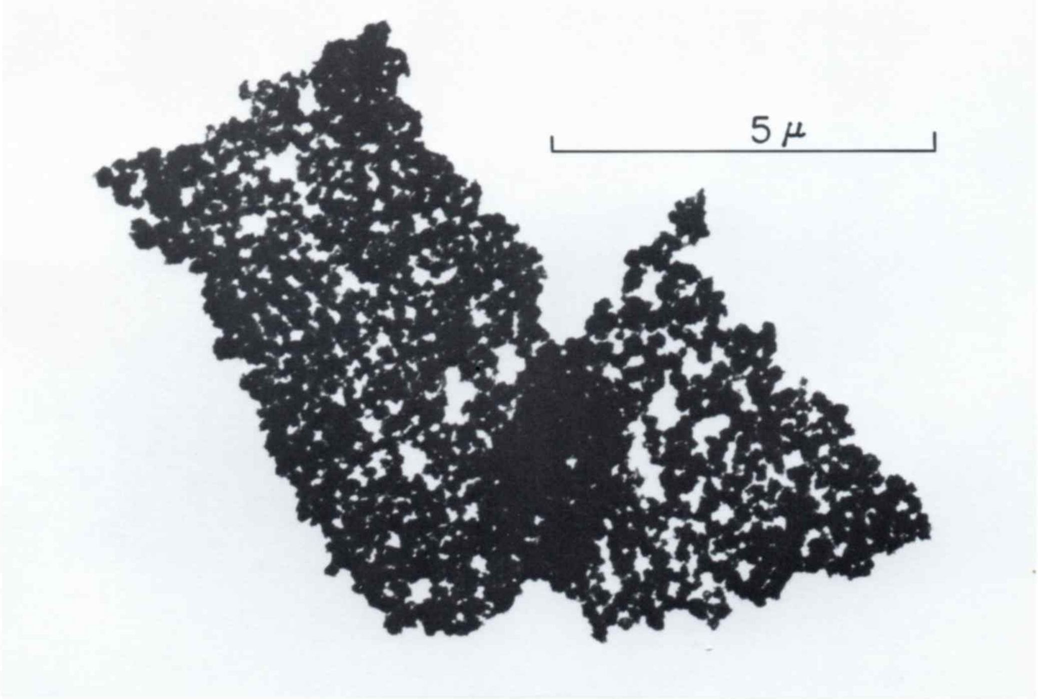


Fig. 12-53b. Type 107 positive image silver removed from a maximum density region and treated with hydrofluoric acid to remove silica from the interstices; the aggregates are sufficiently interconnected to remain in "flakes." This figure illustrates the concept of the metallic network that leads to the neutrality of Type 107 images at all densities.

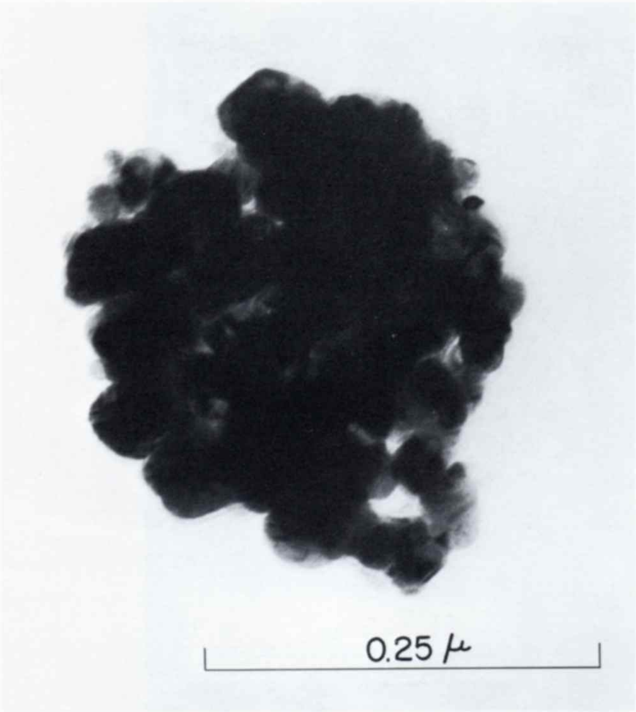


Fig. 12-54. A single Type 107 image aggregate at high magnification. Aggregates average 150 to 300 nm in diameter, and each comprises about 40 closely associated fine particles, which are individual crystals of silver.

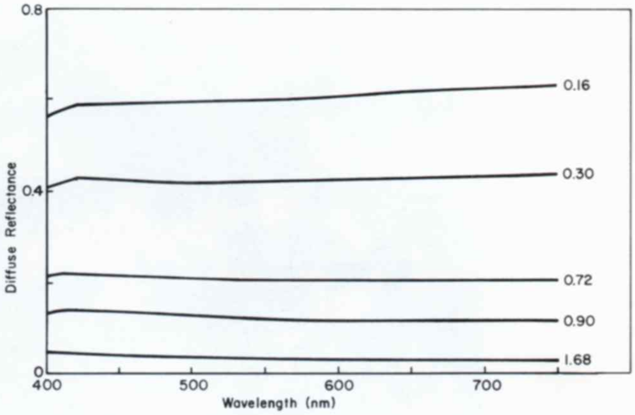


Fig. 12-55. Reflectance spectra of Type 107 images over a wide density range. The neutrality of all densities, as shown by these curves, was a terminal product of research from 1944 to 1950; the system has been in use in the basic black and white product from then to the present (1976). Since the curves are flat over the visual range, each can be characterized by a single reading of diffuse reflection density. These densities are shown to the right of the curves.

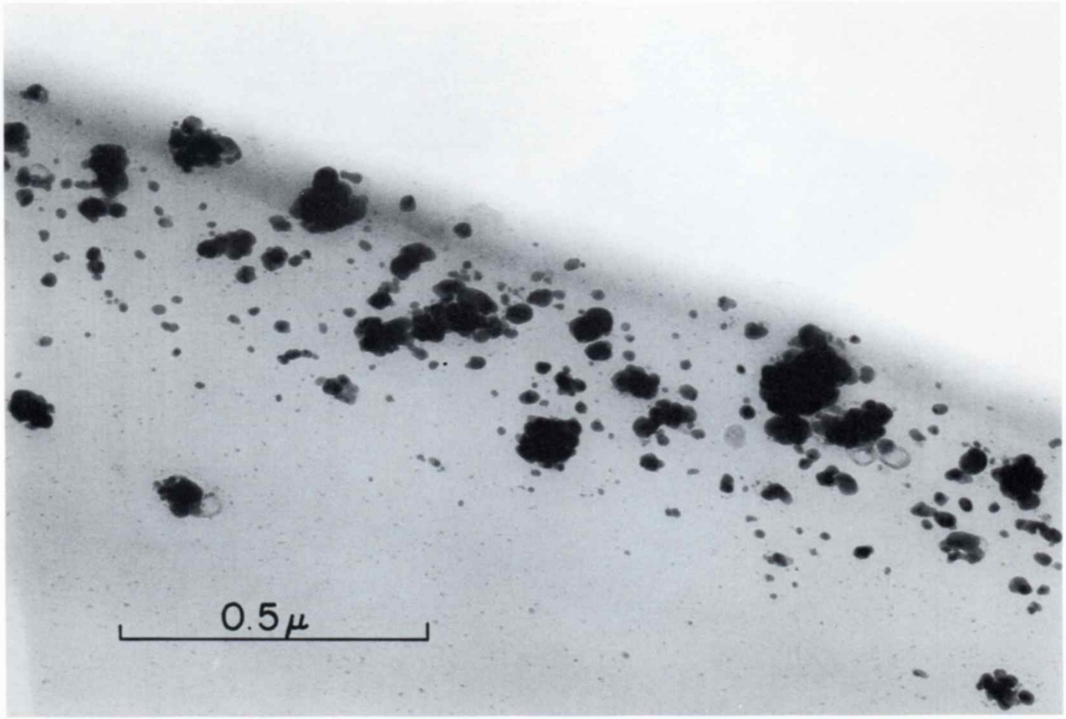


Fig. 12-56. Cross section of an image in regenerated cellulose (Type 87). The depth of the image is approximately the depth to which the layer of cellulose has been regenerated.

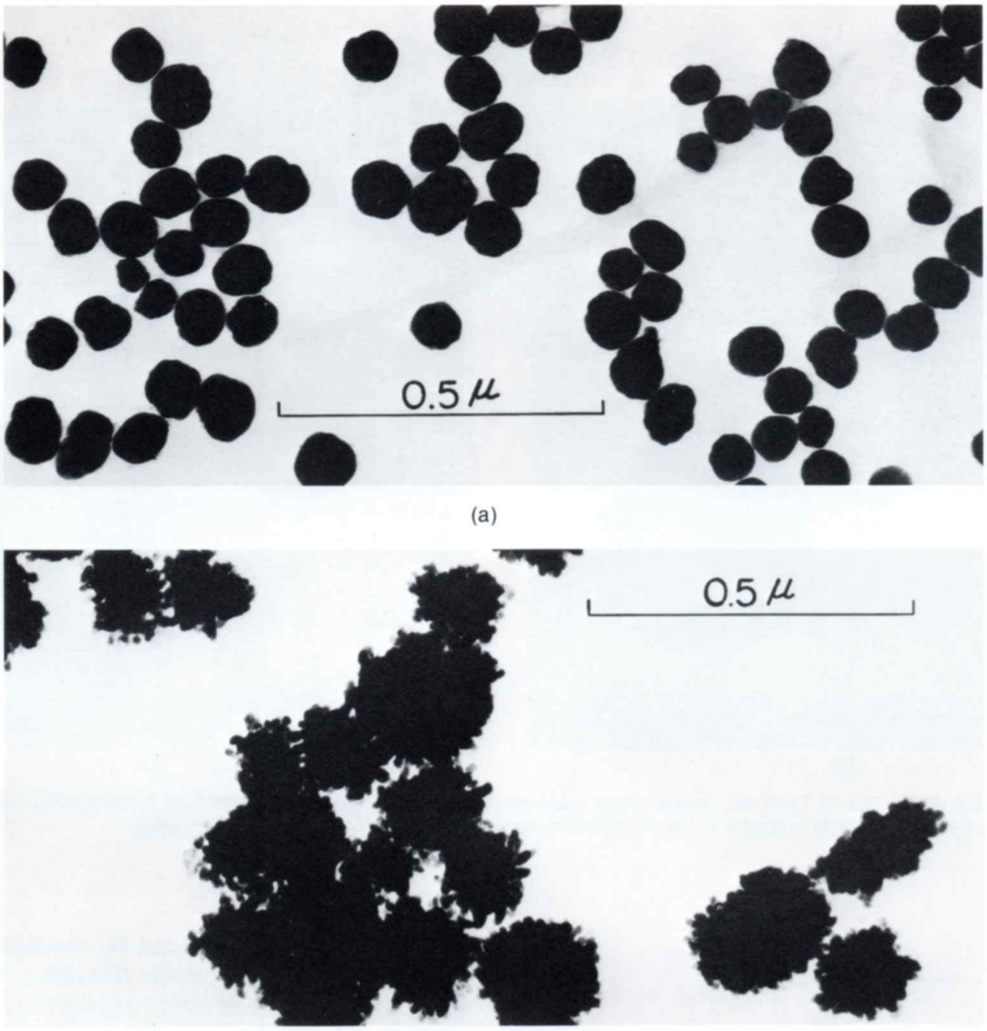


Fig. 12-57. Transparency image deposits: (a) brown image formed in mercaptan-free reagent; and (b) black image formed in reagent containing cysteine.

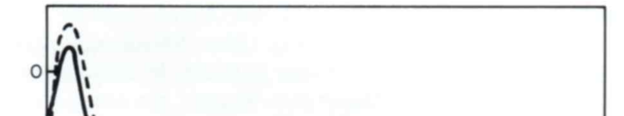
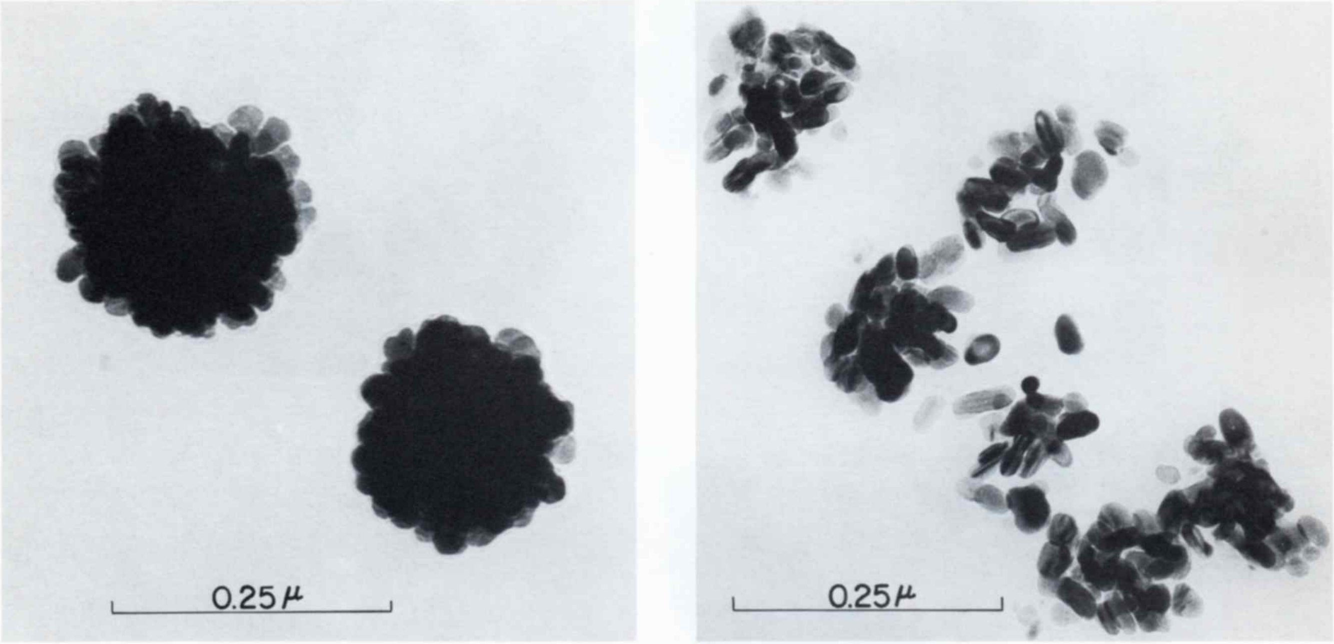


Fig. 12-58. Transmission spectra of brown image (dotted line) and black image (solid line) of Fig. 12-57. Range of diameters of particles and aggregates is indicated over each curve.

Nucleation in Viscous Reagent. The blotting paper, regenerated cellulose and siliceous networks described above all provide environments in which the large single crystals can be aggregated or the aggregates of very small single crystals can be aggregated to satisfy the requirements for blackness; and in these environments the precipitation of the image in the desired state is achieved with remarkable independence of the chemistry of precipitation. In general, the most primitive reduction of silver ion is all that is required. When these environments or their equivalent are not available—for example, when the image is to be precipitated in the viscous reagent—simple precipitation will lead to single crystals too small and too far apart to satisfy the large single crystal condition, but too large to enter into spontaneous clustering. Figure 12-57a shows such a deposit.

In the black and white transparency systems in which a viscous reagent containing nuclei becomes the matrix for growth of image aggregates[47] (Types 46L and 146L), the formation of small particles which readily form



(a) (b)

Fig. 12-59. (a) Single agregates of Type 46L image silver washed free of polymer (120 keV electron micrograph); (b) aggregates like those shown in (a) sectioned while in place in the finished image layer (200 keV electron micrograph).

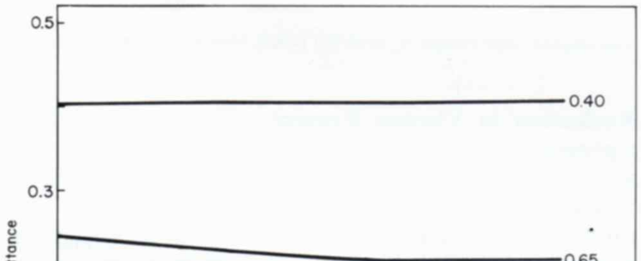
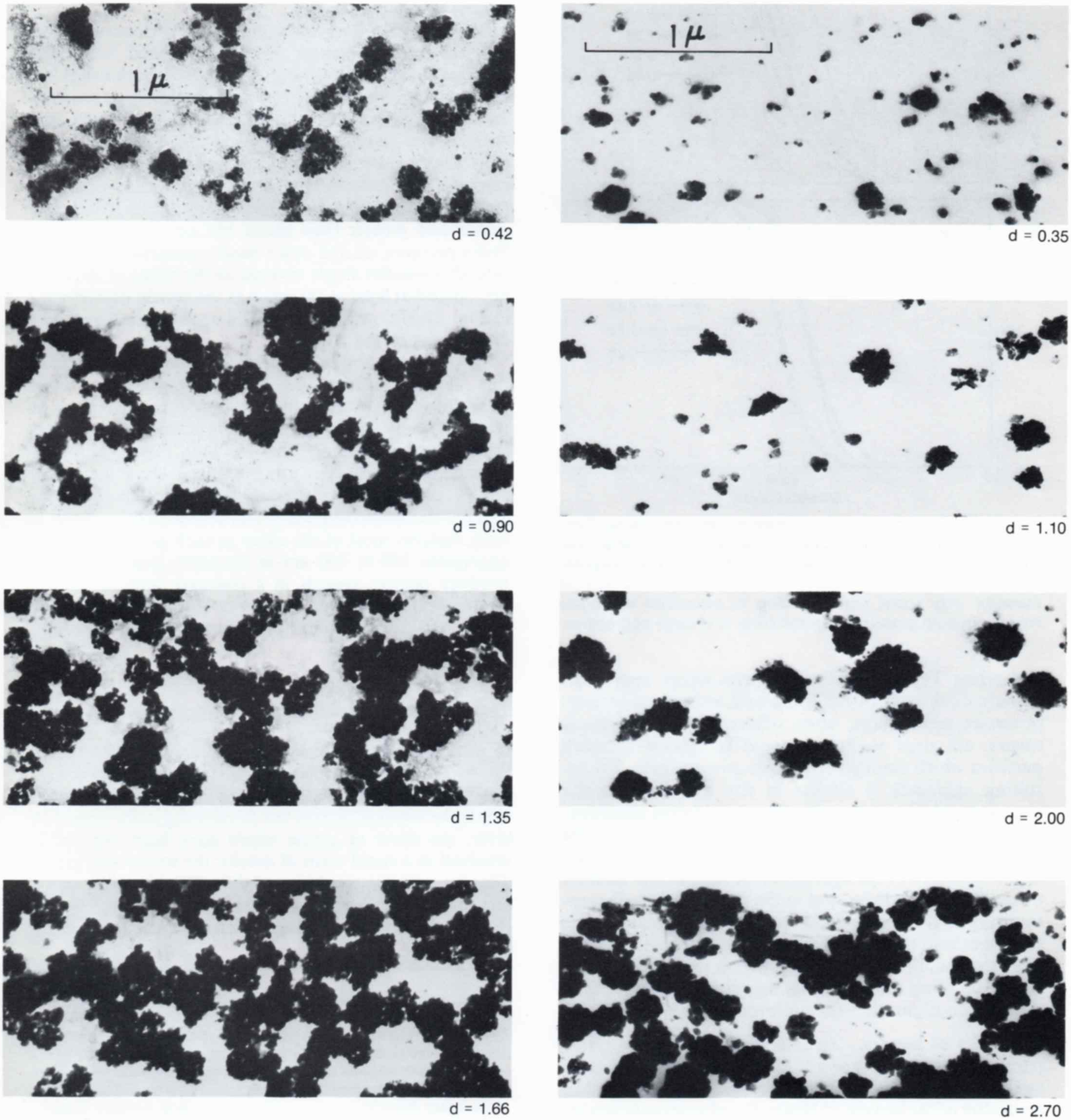


Fig. 12-60. Transmission spectra of Type 46L transparency images at several densities. Since the curves are flat over the visual range, each can be characterized by a single reading of diffuse transmission density. This density is indicated to the right of each curve.

"large" aggregates is assisted by mercaptans included in the reagent. To demonstrate this effect, Fig. 12-57 compares the structures of image deposits formed in a viscous reagent (a) without and (b) with a mercaptan component.[48,49] The mercaptan-free reagent used as control produced a brown image comprising particles 50 to 100 nm in diameter, many of which appear to be single crystals. A reagent containing the mercaptan cysteine[50] produced a black image comprising 120 to 200 nm aggregates, each including 50 or more fine particles in close association. The spectra of these two images are compared in Fig. 12-58.

The silver aggregates which make up the Type 46L image deposit, shown at high magnification both entire and in cross section in Figs. 12-59a and b, measure 150 to 250 nm in diameter, and each aggregate includes about 50 fine particles 10 to 25 nm in diameter. The extinction bands visible in the fine particles of the sectioned aggregate are indicative of their crystallinity. The transmission spectra of Fig. 12-60 demonstrate the near-neutrality of a Type 46L image over a wide density range.

Although they are formed in a completely different environment, the image aggregates of the transparency positive show a great structural similarity to the black



(a) (b)

Fig. 12-61. "Step wedges" illustrating the approximation to uniformity of aggregates for (a) Type 107 and (b) Type 46L images over the full range of optical densities.

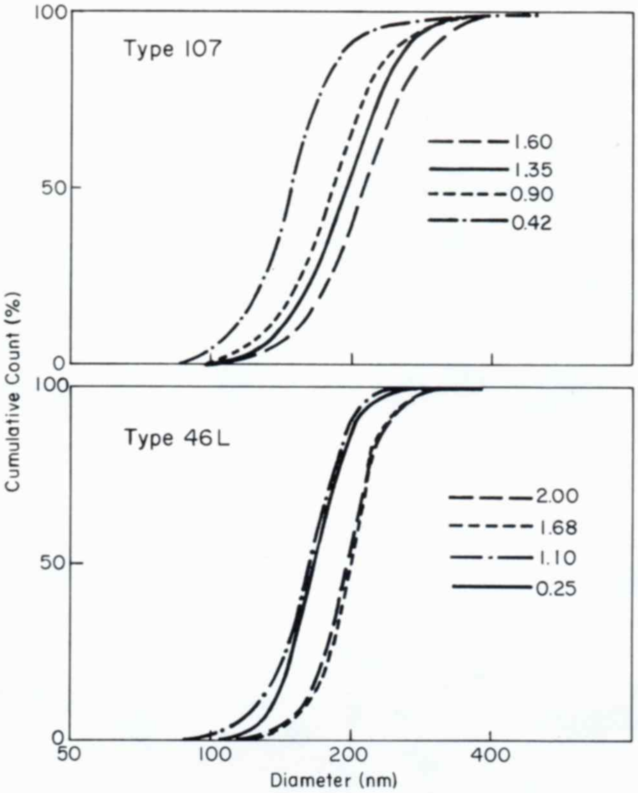


Fig. 12-62. Size distribution of aggregates comprising Type 107 and Type 46L images over a wide range of densities. For each density indicated, cumulative percentages of aggregates, sized from electron micrograph counts, are plotted against diameter (log scale) corresponding to calculated aggregate volume. In both cases most of the silver is in large aggregates.

and white Type 107 reflection print image aggregates already described. In the black and white transparency processes mercaptans, often referred to as blue-black toners, are used to induce rapid formation of small particles which readily collect into an aggregate. The resulting aggregate is similar in size and form to the aggregate which in the reflection print forms spontaneously with or without a mercaptan present.* The dramatic similarity in diameter of the total aggregates, in the structure of the aggregates, in the size and number of constituent particles and in the flatness of the absorption spectra for these two quite different systems supports the hypothesis that the ultimate role of the toner is not to alter the chemical composition within the aggregate but rather to bring into being an aggregate of appropriate size and configuration for uniform light absorption.

Neutrality of Images. In both the reflection and transparency systems the growth of compact arrays of large aggregates (100 nm or more) accounts for the spectral neutrality of the images.** Neutrality of aggregate images requires the fine particles within each large aggregate to be in contact or in close proximity, acting together as a single unit of appropriate size and conductivity; acting individually, the 10 to 30 nm particles would produce yellow or orange images.

The spectral curves and corresponding electron micrographs of the compact images described here have demonstrated a consistent size-color relationship for silver deposits formed in very different thin layer environments. In all cases, from the close-packed single crystals of the 1944 images in α-cellulose blotting paper (Fig. 12-38) to the Type 46L aggregates of 50 or more fine crystals (Fig. 12-59), the images are black when the crystals or aggregates of crystals are tightly packed together and greater than about 100 nm in diameter.*** Sepia pictures, on the other hand, comprise either considerably smaller single crystals, in the range of 50 to 100 nm, spaced at least as far apart as the crystal diameter (as in Fig. 12-57a) or loosely packed aggregates of very fine crystals (as in Fig. 12-49).

In the black and white processes consistently neutral hue at all densities is achieved by producing large particles or aggregates over the entire density range, as illustrated by the micrographs of aggregates from representative steps of Type 107 and Type 46L images presented in Figs. 12-61a and b, respectively. Figure 12-62 shows corresponding size distribution curves of the aggregates comprising images at several density steps. In both systems most of the silver at each density step is in aggregates 150 to 300 nm in diameter, large enough to produce neutral spectra in a compact layer; the small aggregates included at the lower densities account for only a very small amount of silver and do not materially affect the absorption.

The Fate of Silver During Processing

In silver transfer processes leading to positive images, the silver of both exposed and unexposed grains undergoes development concomitantly in different strata. While the exposed grains are developing in the emulsion layer, the silver of grains which have been exposed is involved in a rapid train of events: the unexposed grains dissolve, and the resulting soluble silver complex transfers to the receiving layer, where it immediately develops to form the crystals of silver which comprise the positive image.

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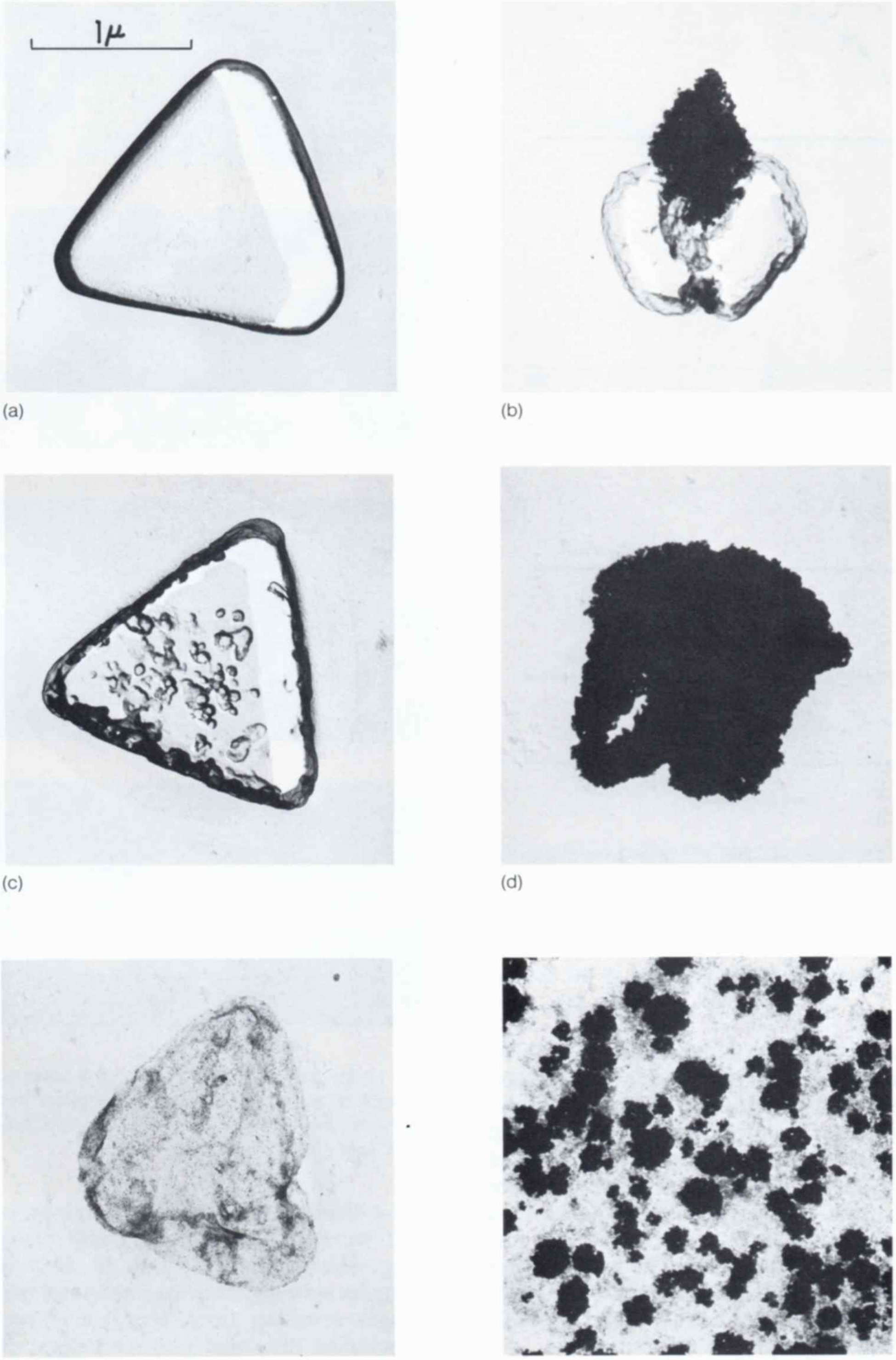
*The effect of mercaptans in this process is unlike that characterized by Cassiers, who described a mercaptan-induced shift from brown to black in Gevacopy transfer images comprising silver particles of approximately 65 nm in diameter. Cassiers reported that this color shift was accompanied by changes of crystal order and surface crystalline state, with no significant change in overall dimension or distribution of silver particles.[51]

**This observation is based on the correlation of microscopic and spectrophotometric data. Calculations based on the classical Mie equation for scattering and absorption by isolated metallic spheres, often useful in characterizing the optical properties of loosely packed silver image deposits,[52] are not applicable to these compact images.

***A 1962 paper of Weyde, Klein and Metz[53] describes shifts from brown to black for silver deposited in thick gelatin layers as the packing density of silver is increased. The color shift is attributed to increasing incidence of twin- and triple-particle aggregates of particles; the illustrations show that even their most densely packed deposits are much more dilute and much less aggregated than the compact deposits discussed here.



(a) (b) (c) (d) (e) (f)

Fig. 12-63. Stages in processing of Type 107 grains: (a) is replicated from an unexposed undeveloped grain, (b) and (c) from grains processed 1/10 sec; (b), an exposed grain, is partially developed; (c), an unexposed grain, is partially dissolved; (d) is a fully developed grain; (e) the imprint of a dissolved grain as it appears after the gelatin is removed; (f) is positive image silver derived from a single grain such as (a) and transferred to an image-receiving layer, shown at the same magnification as the negative grains (a) through (e).

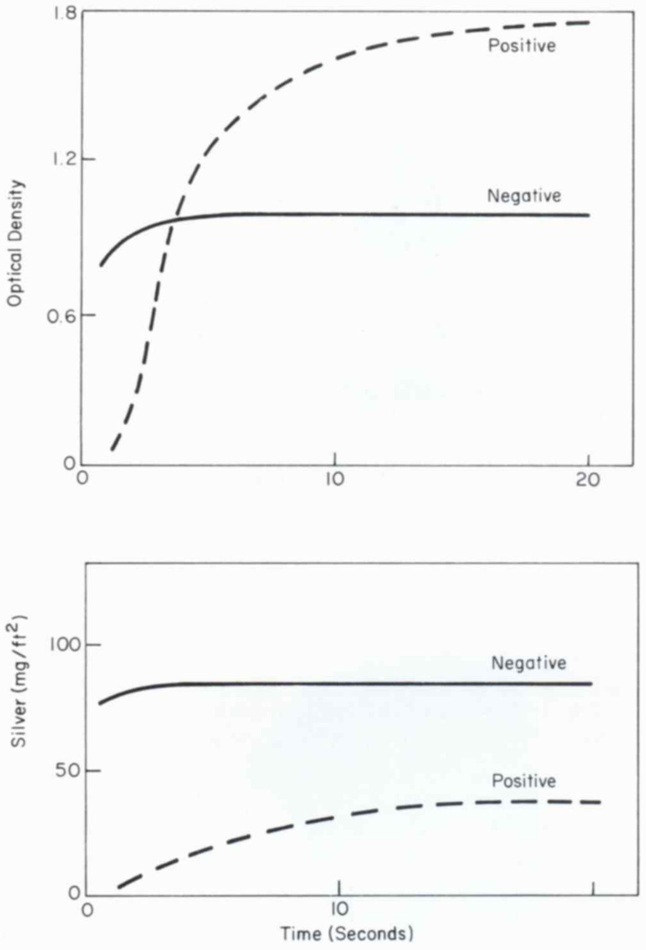


Fig. 12-64. Rates of formation of Type 107 negative and positive image deposits. The upper curves show image growth in terms of optical density, and the lower curves show growth of the same images in terms of the amount of silver developed. Comparing the two dotted lines, on the one hand, and the two solid lines, on the other, note the greater covering power of the positive silver.

Image Formation in the Type 107 Process. The electron micrographs of Fig. 12-63 illustrate the changes which take place in individual silver halide grains as they participate in the formation of negative and positive images in the Type 107 process. The exposed grains show appreciable development after only 1/10 sec and full development within 15 sec; the unexposed grains show considerable etching after 1/10 sec and leave only empty "shells" after 15 sec. The final figure of the series is a micrograph of the central portion of the deposit of positive silver derived from a single Type 107 grain. (See also Fig. 12-73c.)

The rapid deposition of Type 107 negative and positive silver is further illustrated in Fig. 12-64, which shows the rates of formation of negative and positive images of maximum density in terms of both optical density and silver coverage. Each image reaches asymptotic values within 20 sec. Figure 12-65 shows maximum density areas of the positive image at several stages during its growth.

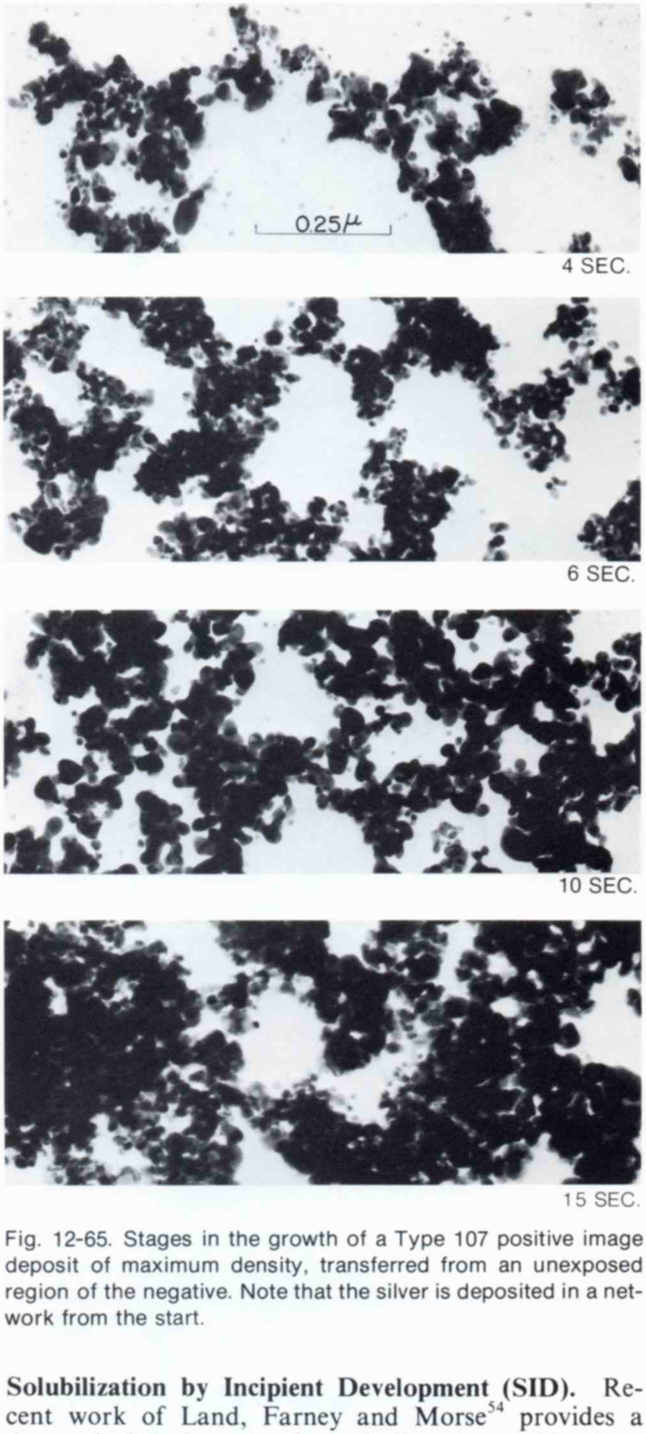


Fig. 12-65. Stages in the growth of a Type 107 positive image deposit of maximum density, transferred from an unexposed region of the negative. Note that the silver is deposited in a network from the start.

Solubilization by Incipient Development (SID). Recent work of Land, Farney and Morse[54] provides a deeper insight into the fate of silver in soluble silver complex systems. They had observed that weak negative images resulting from very low exposures often accompanied the usual positive images of the black and white transfer processes, as shown in Fig. 12-66. Land suggested that the weak negative image could form only if the slightly exposed grains were rendered preferentially soluble during early development.

The phenomenon, designated "Solubilization by Incipient Development," is enhanced by reagents which include both a high solubility (HS) ligand and a low solubility (LS) ligand for silver ion. The HS ligand is

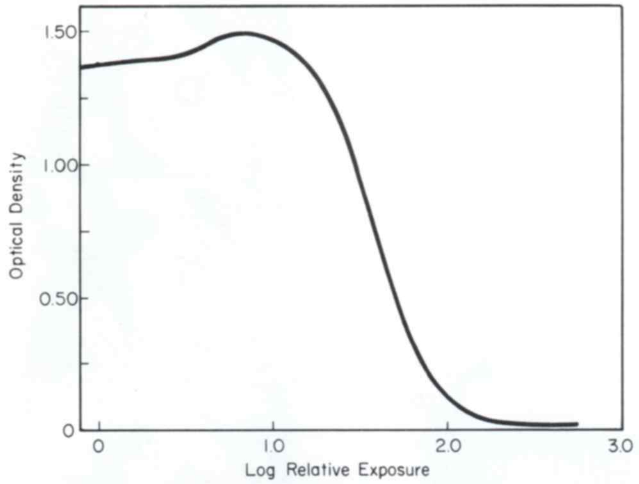


Fig. 12-66. *D vs.* log *E* curve of Type 107 transfer image showing, in addition to a normal positive, a weak negative image at very low exposure level.

defined as a compound—such as hypo—which forms a highly water-soluble complex and the LS ligand as a compound—such as 1-phenyl-5-mercaptotetrazole (PMT)—which forms a sparingly water-soluble complex or salt with silver ion. In the presence of such a pair of ligands and the developing agent, grains which have received low level exposure may be more readily dissolved than either the unexposed grains or the more fully exposed grains, so that a negative image may be transferred.

The development of the slightly exposed grains was found to be characterized by the violent extrusion of filamentary silver from a single development center, as shown in Fig. 12-67; the rest of the grain is propelled in the opposite direction, fragmented and readily dissolved without reduction. Since the soluble silver complex is formed at a distance from the developing filaments, it is not reduced; it is free to diffuse towards whatever nucleating system is made available to it and to give up its silver by reduction upon arriving at these nuclei.

With grains which receive more exposure, development originates at multiple centers, which serve as nuclei at the original site of the grain. The amount of silver that is reduced while in contact with already reduced silver increases with the amount of exposure the grain receives. Furthermore, the hydromechanical thrust in any one direction is balanced by thrust in other directions, with the net result that few complexed ions are freed to diffuse from the original site.

Whether transfer of a negative or a positive image prevails in SID processing depends on the relative concentrations of the two ligands, processing time and exposure level as shown in Figs. 12-68, 12-69 and 12-70, respectively. As the weakly exposed grains are the ones used in the negative transfer process, the effective film speeds are high. Equivalent ASA speeds up to 20,000 are obtainable. Figure 12-71 shows negative and positive images produced with emulsion and reagent of identical composition, using camera exposures five stops apart, as described by the curves of Fig. 12-70.

The following working hypothesis was supported by the experimental data derived from tests with many ligands and a variety of emulsions, from single grain observations and from reaction rate studies:

> PMT, an LS ligand, coats all grains with a sparingly soluble layer, and this impedes their dissolution by the thiosulfate, an HS ligand.
>
> The negative transfer image comes about for two reasons. First, during the period allowed for the developer to act, unexposed grains will not dissolve because a sparingly soluble crust forms around them. Second, one has to assume that as development begins on weakly exposed grains, it is not carried to completion but causes the sparingly soluble crust to break open and dissolution of the silver halide to take place: under the quite violent exothermic conditions of development a soluble complex with silver ions is produced. The reason why development of weakly exposed grains is not carried to completion rapidly presumably is that development is slowed down by the LS ligand and that the soluble complex formed is not readily reducible. Therefore the dissolved complexed silver ions can get away from the donor grains without being reduced and diffuse to the receptor sheet where they are reduced to metallic silver at the nuclei.[54a]

The fact that hypo alone can, under carefully controlled conditions, be made to produce the SID phenomenon suggests that a single complexing agent is all that is required and that an HS and LS ligand pair—e.g., PMT and hypo—produce a mixed complex or a mixture of complexes which forms a crust with just the right low solubility characteristics.

Reference 54a also discusses SID as a participating mechanism in other development processes. The phenomenon was readily produced with all of the many emulsions and developing agents tested. Furthermore, the latent image utilized in the SID process gave every evidence of being the ordinary latent image. It was very similar in reciprocity failure characteristics, in effective film sensitivity and in stability at both room temperature and 120° F to the latent image operative in the positive image transfer process with the same emulsion.

Process Symmetry. In both the SID processes and the conventional positive silver transfer processes, final disposition of the silver depends upon a balance among rates of the several concurrent reactions. Such balance also facilitates consistent performance over a wide range of temperatures, as was recognized in the earliest work. Figure 12-72 from Ref. 1 shows the symmetry of negative and positive development rate curves at 30 and 70° F for the Type 40 process.

The cyclic use of silver halide solvent is a significant means of achieving balance between the rates of dissolution and development of silver halide grains in the emulsion. With hypo the cycle is effected by the release of thiosulfate ion as silver is precipitated from the soluble complex in the image-receiving layer, making the thiosulfate ion again available as a solvent so that it may

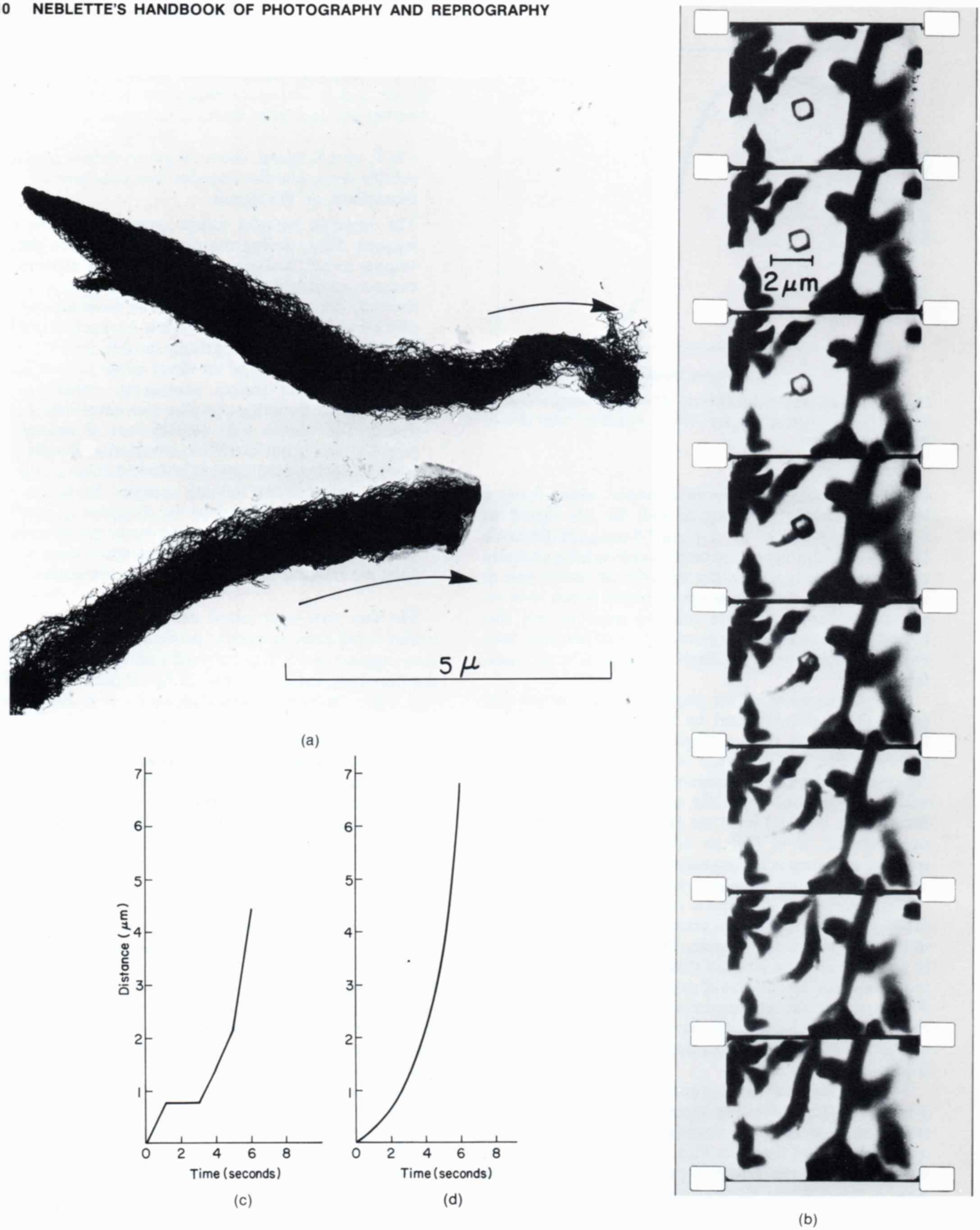


Fig. 12-67. (a) Silver halide grains developed under SID conditions. Fine threads of silver are about one nm in diameter. During development each grain moves with considerable force, leaving in its wake a growing mass of threads. The arrows show the direction of motion, observed by infrared cinemicrography, of the developing grains. (b) Cinemicrographic frames showing progressive stages in the SID development of a single grain. The interval between frames is 1 sec. (c) Travel of the developing grain of Fig. 12-67(b). The grain's velocity as it left the field of view was approximately 2.3 μm/sec. (d) Rate of growth of the mass of filaments extending behind the developing grain of Fig. 12-67(b).

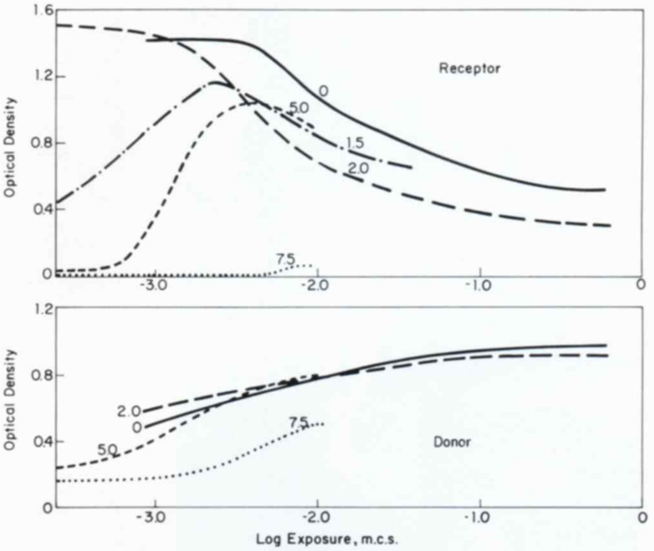


Fig. 12-68. Family of curves demonstrating transition of image in the SID receptor sheet from positive to negative with increasing ratio of PMT to hypo in the reagent. Hypo is held constant as PMT is varied; numbers on curves indicate concentration of PMT in mg/ml reagent. The donor is the light-sensitive emulsion layer, and the receptor is the layer to which dissolved silver is transferred. In this case the donor image is formed in a layer with a large excess of silver halide over what is required to form the receptor image, and the positive donor images corresponding to the negative receptor images cannot be discerned.

dissolve and transport more silver. The cyclic use of the thiosulfate ion makes possible efficient silver transfer with a minimum concentration of hypo in the reagent; even more important, it facilitates precise control of the relationship of rate of transfer and rates of development in both negative and image-receiving layers and hence leads to precise control of speed and characteristic curve shape. Hypo concentrations may be as little as 0.25 times the stoichiometric equivalent of the transferred silver.

Lateral Diffusion; Resolution. Resolution of the positive images resulting from transfer of soluble silver complex is a function of both the initial resolving power of the emulsion used and the lateral diffusion of image-forming silver during the transfer process. The lateral diffusion of the image in soluble silver is, of course, minimized by increasing the rate of precipitation relative to the rate of ionic diffusion, by decreasing separation between the emulsion and the receiving layer, and by restricting the thickness of both the emulsion and the receiving layer.

The diffusion which does occur is shown in the micrographs of positive images resulting from the transfer of single isolated grains to preformed receiving layers, Fig. 12-73a, b and c. Images (a) and (b), both transferred from 0.8 μm grains, differed in the distance between emulsion and receiving layer at the start of transfer, in case (a) the maximum distance being less than 3 μm and in (b) approximately 15 μm. The diameters of the two transferred images differ approximately in proportion to these distances. These well-resolved positive image "fields" give an indication of the fates of individual grains

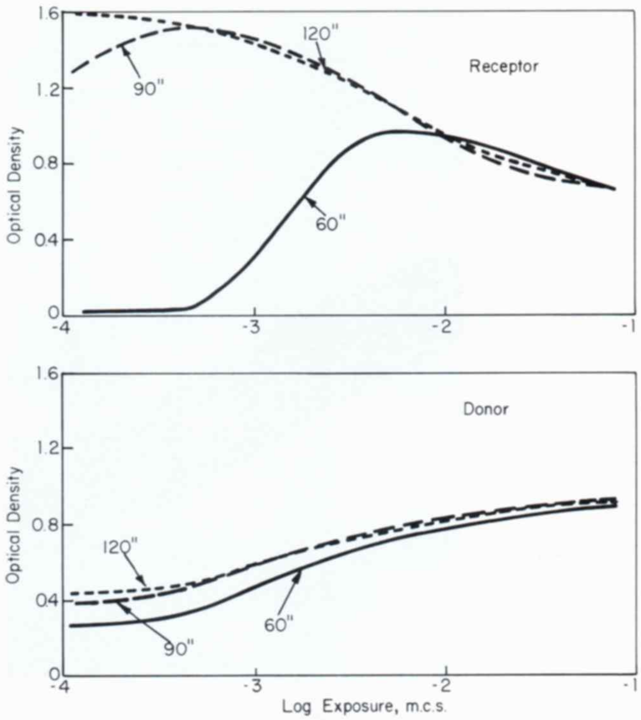


Fig. 12-69 *D vs.* log *E* curves for SID donor and receptor sheet images for a range of imbibition times. Note the take-over of positive image formation in the receptor as imbibition time increases.

The ejected ions form complex in solution, whereas the grain, being coated with a crust of the complex, cannot dissolve until the crust dissolves. The finite time required for this dissolution permits a negative to be formed by abstracting the silver ions in complex form from the exposed grains during the time that precedes the dissolution of the silver halide in the exposed grains, protected as it is by the crust. At the end of this finite time, however, the crust will have been dissolved and the unexposed grains will go into solution to be transferred and precipitated, forming a positive in the same surface in which the negative had been formed. Depending on the mass of silver halide in the donor originally, the densities of the positive may dominate those of the transferred negatives. Thus, with short times of imbibition the receptor will have received the silver for a negative; with longer times, enough silver for a *net* positive.

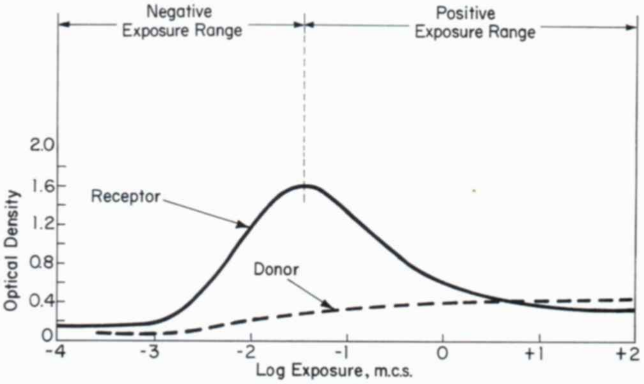


Fig. 12-70. *D vs.* log *E* curves of SID images in donor and receptor sheets over a wide range of exposures, using a single reagent and hence a single ratio of PMT to hypo.

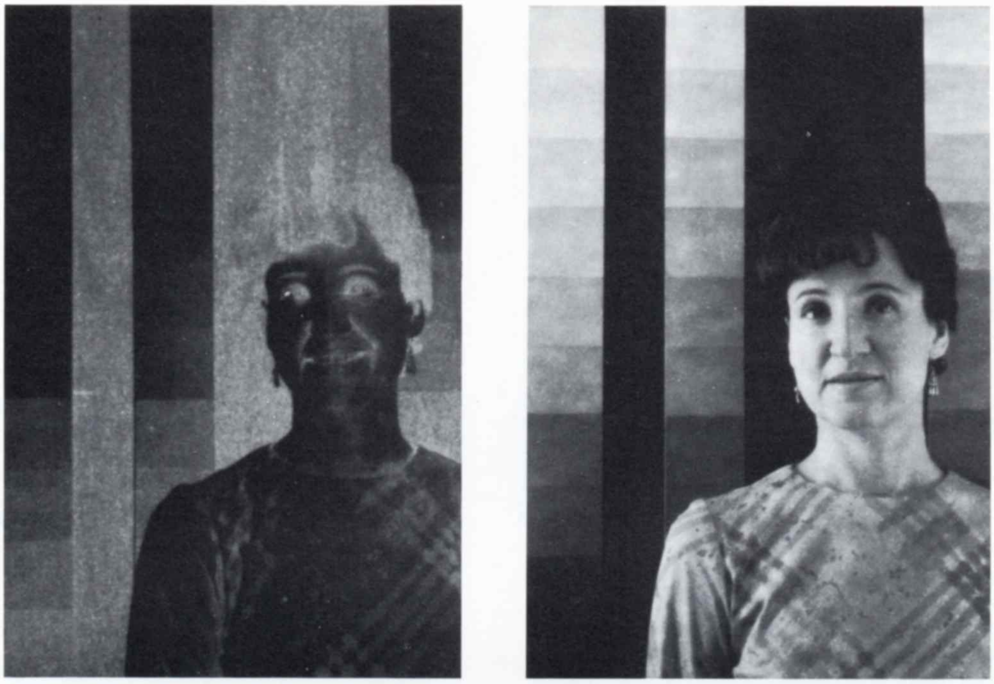


Fig. 12-71. Negative and positive SID transfers produced with identical components, but with in-camera exposures differing by five stops. See also Fig. 12-70.

in silver transfer systems with emulsions of normal con-concentrations. Image (c) is from a somewhat larger grain of Type 107 emulsion coated and processed as was (b), with initial separation approximately 15 μm. The broad distribution of grain sizes characteristic of this emulsion makes it impossible to designate the diameter of the grain which yielded image (c). This image nevertheless is an example of the pattern of positive silver derived from a larger single grain.

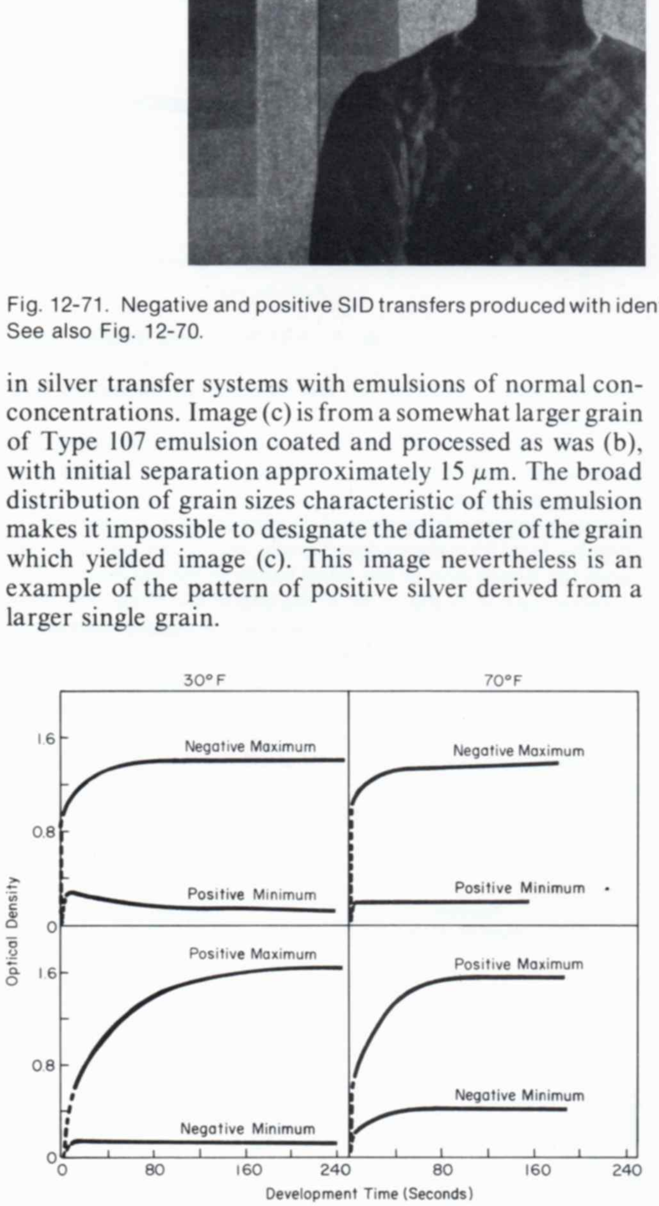


Fig. 12-72. Growth of Type 40 (sepia) positive and negative images in both maximum and minimum exposure regions, at 30°F and at 70°F. (The difference of covering power between negative silver and positive silver does not show because the mass of silver chosen for the negative in the Type 40 process is far greater than the amount transferred for a good positive.)

The Type 46L transparency images, which form in the reagent layer with moderate lateral diffusion, resolve 32 to 35 line pairs/mm, and Type 107 reflection print images 22 to 28 line pairs/mm. The resolution of an image which has undergone very little lateral diffusion, as in Fig. 12-73a, is as high as 200 line pairs/mm or more.

Efficiency of High Speed Films.* The high speed films take particular advantage of the rapid and efficient extraction and deposition of transferred silver by using, in conjunction with a highly sensitive negative, developing agents which are extremely active at high pH. Much of the silver halide, exposed and unexposed, would develop if left too long in such a vigorous reducing environment. The unexposed silver halide is simply dissolved, transferred and redeposited before it can be reduced to fog in the emulsion layer. The process thus involves a critical rate of fog development, in addition to the critical rates of negative image development, silver halide

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*Polaroid 3000 Film (Types 47, 107, etc.), rated at ASA equivalent speed 3000, is the fastest material available for general purpose photography. It was the first film fast enough to permit the great depth of field afforded by very small apertures—as low as *f*/90—in a format producing pictures large enough for direct viewing. The high speed film makes it practical to take pictures indoors by available light, as well as outdoors over a wide range of lighting conditions, and to stop motion with a rapid shutter at high light levels. Its speed has also made the 3000 film very important for many scientific applications; Figure 25 describes many such uses. Examples of photographs made possible by the high speed film are shown in Figs. 12-26 and 12-74.

An ultrahigh speed film, the high contrast Polascope (Type 410) for rapid oscillograph trace recording, is rated at equivalent ASA speed 10,000; it is a special-purpose film capable of recording cathode ray tube transients too rapid to be discerned by eye, as shown in Fig. 12-26e, and effective at extremely low light levels.

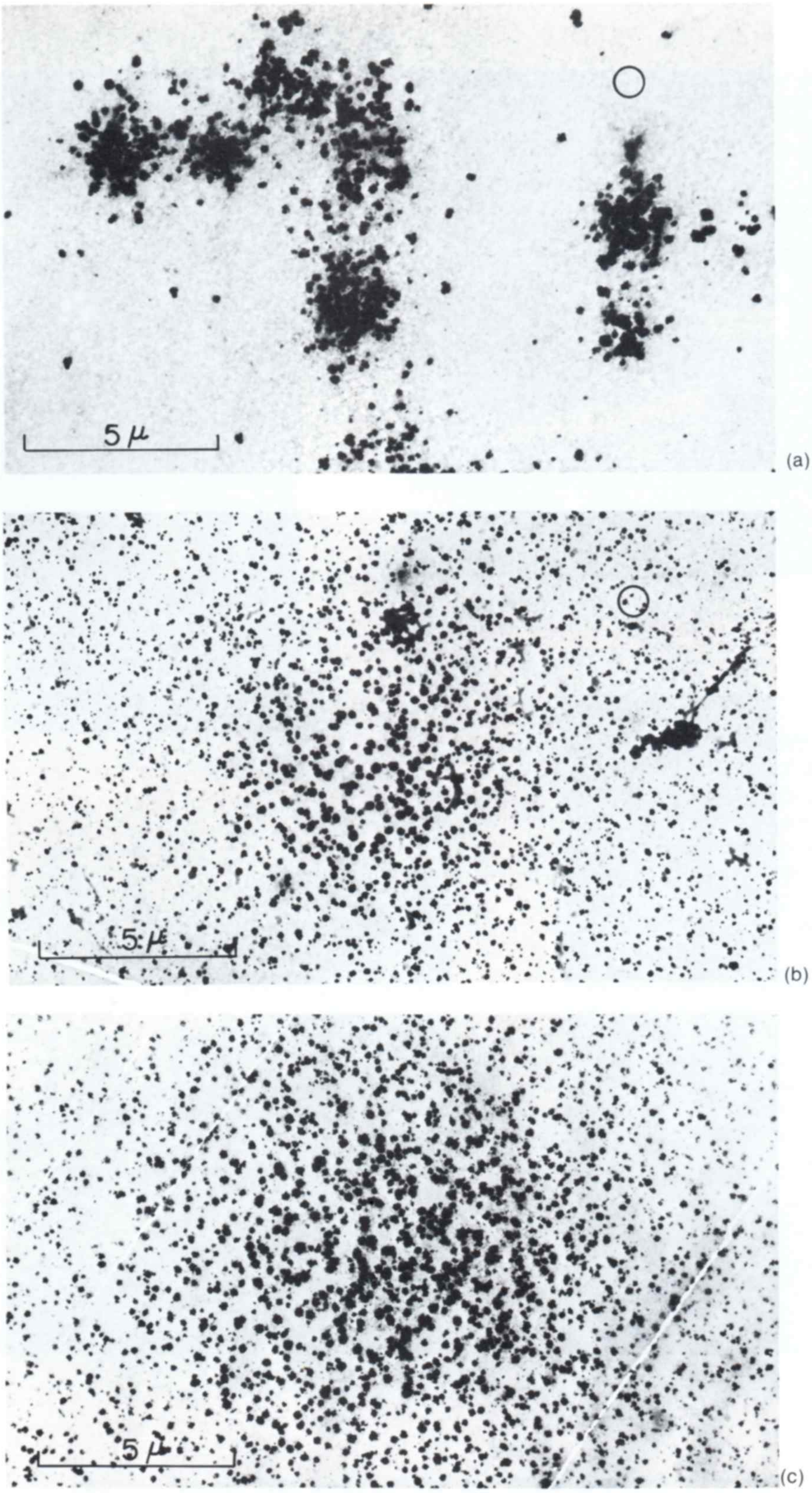

Fig. 12-73. Positive images transferred from single grains, isolation of the grain being obtained by using very dilute emulsion layers. Maximum distance between emulsion and receiving layer was 3 μm for (a), in which the emulsion was coated directly over the receiving layer, and 15 μm for (b) and (c), where the emulsion was on a separate support. The emulsion used for (a) and (b) had uniform grains of 0.8 μm diameter. (c) is from an emulsion with grains of larger size and broader distribution than the one used for (a) and (b). The circles represent the diameter of a single grain in the negative before development.

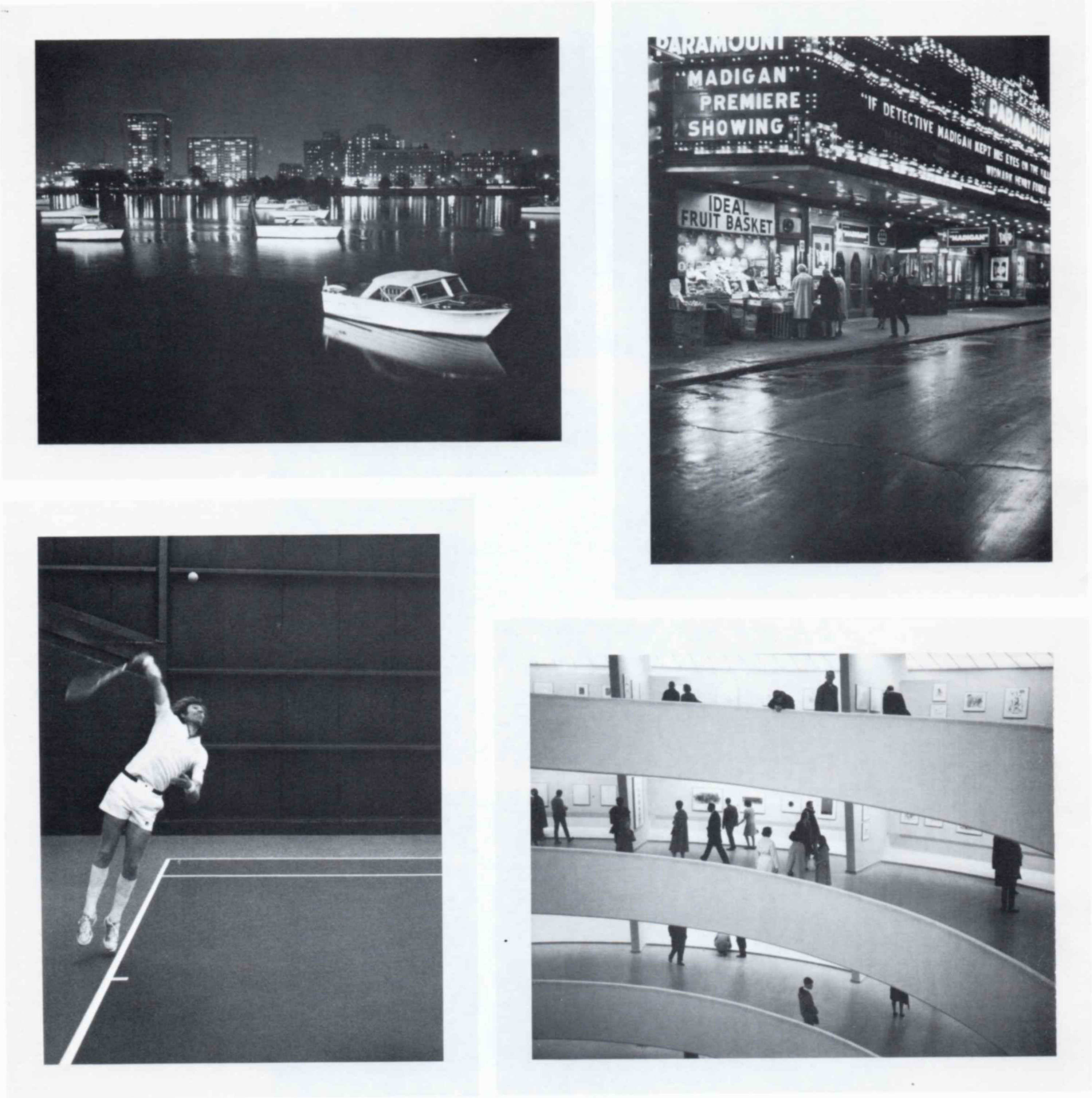

Fig. 12-74. Photographs with Type 107 film, speed 3000. See also Fig. 12-26.

dissolution, and positive silver image deposition. The entire process can be completed in as little as five seconds.*

Figure 12-75 shows the characteristic curves of Type 107 negative and positive images; both optical density and silver coverage are plotted against relative log exposure to illustrate the difference in covering power of the two silver image deposits. (See also Fig. 12-64.) Covering power—i.e., ratio of optical density to mass of silver per unit area—is seen to relate inversely to unit particle size. The positive silver image, which is high in covering power, comprises a very thin layer of aggregates, forming a mattresslike continuum at high densities, as shown earlier in Fig. 12-53b. The negative image, which is low in covering power, is made up of the somewhat expanded developed grains of the original emulsion, as in Fig. 12-63d, which are about ten times as great in diameter as the positive image aggregates. Because the covering power of the positive silver is high, a useful image is obtained with relatively little silver. The negative itself can therefore contain much less silver than would ordinarily be required to produce a useful negative by tank processing, and the effective speed of the film is enhanced by the efficient utilization of silver halide in the thin emulsion layer.

Design of Positive/Negative System (P/N). The design of a material suitable to produce simultaneously both a permanent negative suitable for making enlargements of high quality and a useful transfer positive** required selection of an emulsion of covering power properties different from those of Type 107. Not only must the amount of silver be appropriate for making a good positive image; here the negative grains upon development must also be of appropriate size and covering power to achieve a useful negative curve with the same amount of silver. The emulsion thus chosen is relatively fine-grained. Figure 12-78 compares the grain size distributions of the Type 107 and Type 55 P/N negative emulsions. The mean diameters are 1.01 and 0.36 μm, respectively. The projected area of a fully developed grain of a 55 P/N negative is approximately 0.4 μm^2, or about one-eighth that of the developed grain from Type 107 negative shown in Fig. 12-63d. Figure 12-79 shows characteristic curves of a 55 P/N positive and negative image pair in both optical density and silver; the positive silver covering power is similar to that of the Type 107 positive, and the negative curve shows significantly higher covering power than that of the Type 107 negative.

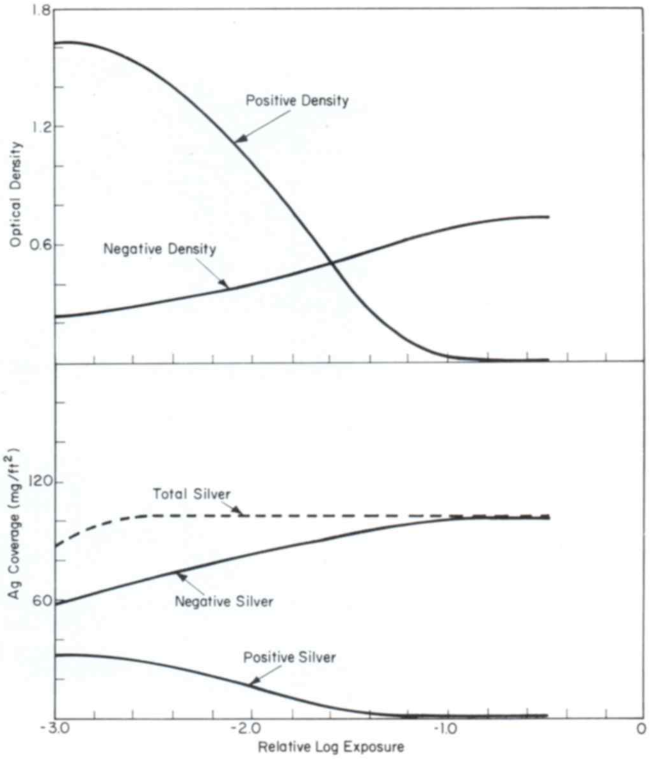

Fig. 12-75. Positive and negative curves, Type 107 film. The upper curves show optical reflection densities and the lower curves show the mass of silver required for each of these densities. Note the relatively small mass of positive silver required to produce the high positive density and the relatively high mass of silver involved in producing the low negative density.

Image Stability

An important specification in the design of the first one-step process was that the print not require washing afterwards to be stable and free from undesired residue or stain. This was a particularly demanding requirement in view of the presence of the concentrated reagent, with its potential for further reaction with image silver and its susceptibility to aerial oxidation.

In most instances the viscous reagent forms a thin layer which adheres to the negative and is removed with the negative when it is stripped from the positive. However, whether or not a layer of reagent is removed, the reagent residual in the image layer must be rendered inert if not already inert. One such technique is to incorporate into the receiving sheet one or more components which will diffuse into the image-bearing layer toward the end of image deposition and decrease the reducing power of the reagent by lowering its pH.[56a]

Type 40 sepia images were stabilized by hydrolyzable esters[56b] and soluble lead salts incorporated in the receiving support. These compounds diffused into the image layer as image deposition reached completion and reacted

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*The accomplishment of rapid processing of the high speed film led to the revision of the reagents for the earlier black and white processes. The processing time for both the 3000 speed film and the Polapan films was reduced from 60 seconds to 10 to 15 sec shortly after the introduction of Polaroid 3000 film in 1959.

**Polaroid Type 55 P/N film, a 4 × 5 in. packet material, yields both a positive print for immediate use and a fully developed and fixed negative of outstanding quality and high resolution (150-165 line pairs/mm). Figure 12-76 shows such a positive/negative pair, and Fig. 12-77 reproduces an enlargement made from a 55 P/N negative. The equivalent ASA speed of 55 P/N is 50, and its processing time is 20 sec. Type 105 P/N, rated at equivalent ASA speed 75, is a positive/negative film in pack format (Fig. 12-31). A removable opaque back coating on the negative sheet permits processing outside the camera.[55]

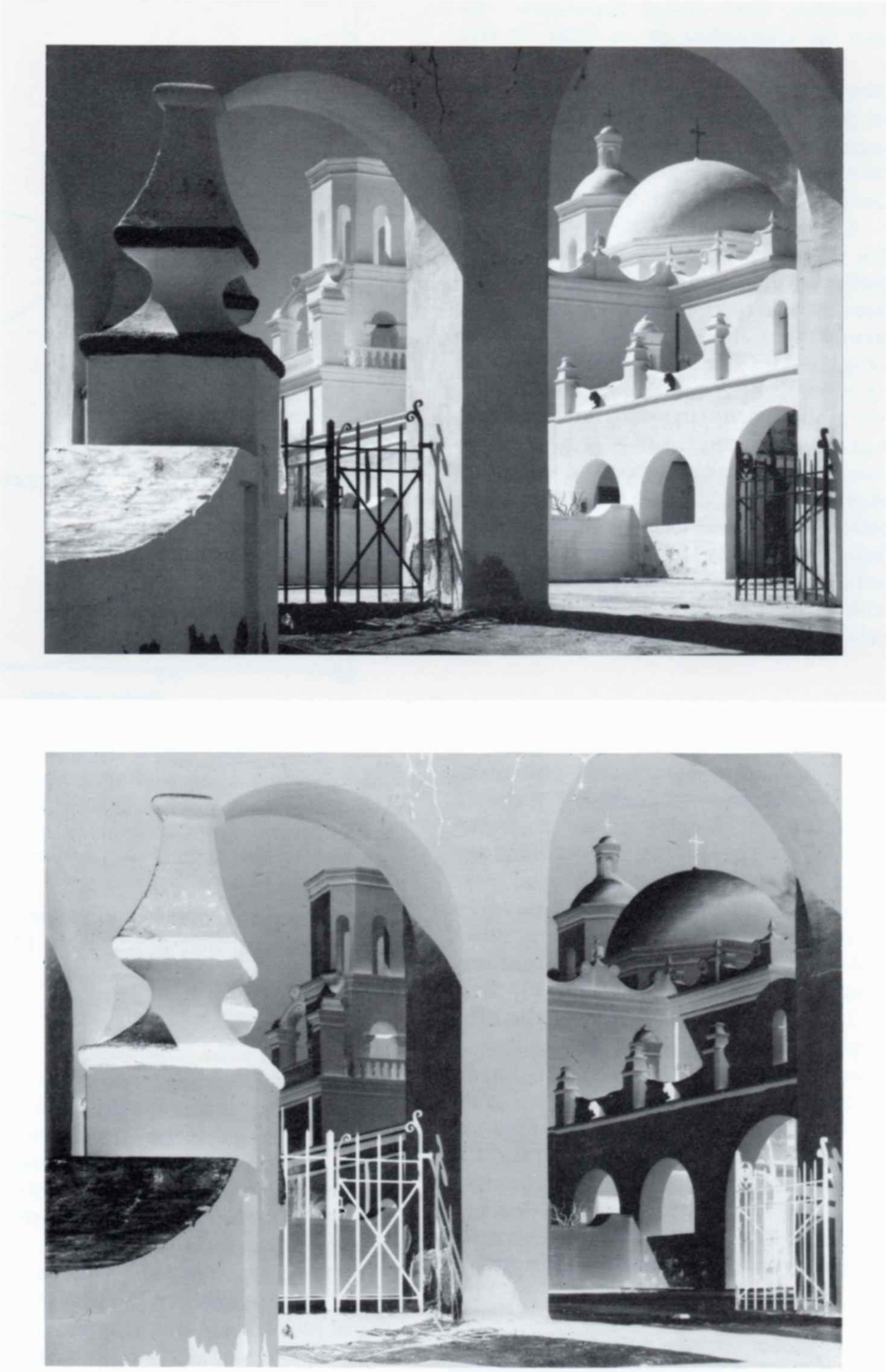

Fig. 12-76. Positive and negative pair, Type 55 P/N. Mission San Xavier Del Bac, Tucson, Arizona, photographed by Ansel Adams (1956).

Fig. 12-77. A gallery print made from a 55 P/N negative. Mission San Xavier Del Bac. See Fig. 12-76.

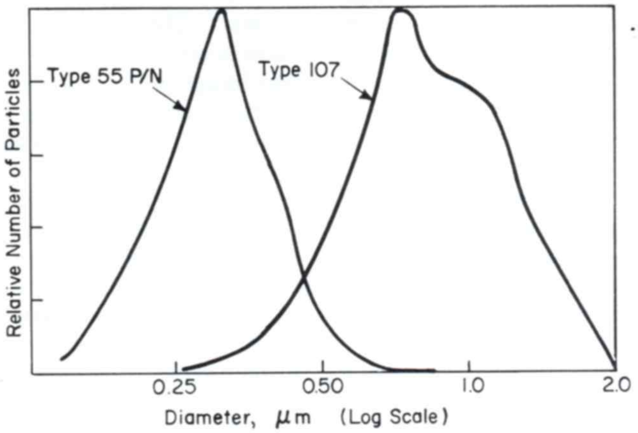

Fig. 12-78. Grain size distributions of Type 55 P/N and Type 107 emulsions.

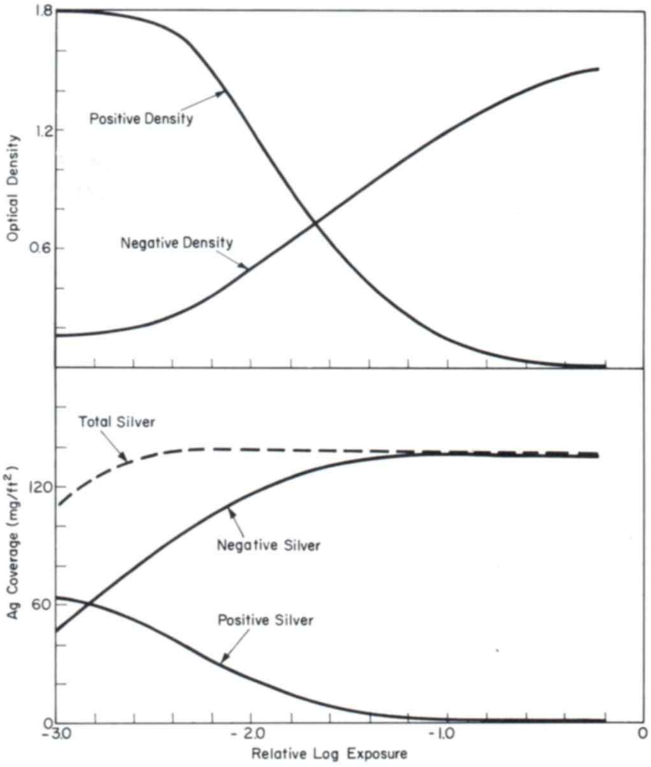

Fig. 12-79. *D vs*. log *E* curves of negative and positive silver, Type 55 P/N. The upper curves show optical transmission density of the negative image and optical reflection density of the positive image vs log exposure. The lower curves show the distribution of silver in the negative and positive images.

with excess alkali, lowering the reducing power of the developing agent and inhibiting formation of its quinone reaction product as well. The lead salt further served as a crosslinking hardener[40] for the polymeric component of the viscous reagent, forming of the reagent a thin, protective layer which remained on the print surface.

The silica receiving layers introduced for black and white images (Type 41) were less readily penetrable by stabilizers incorporated in the paper base, and new structures and techniques were consequently developed. A waterproof layer of cellulose acetate beneath the receiving layer confined both the image and other reaction products to a thin, rapidly penetrable surface stratum. This image layer, which was only about 0.4 μm thick, was readily washed free of residual salts by simple swabbing with water, an instant procedure as compared with the extended washing usually given tray-processed prints. While concentrating the deposit close to the surface made the image easy to wash, its vulnerability to abrasion and to attack by active chemicals in the atmosphere was increased, so that it became necessary to provide protection beyond the removal of residues. Durable lacquers coated from organic solvents protected the image from abrasion but neither removed water-soluble residues nor protected the silver from the atmosphere. Simultaneous coating and stabilization were finally accomplished by using a durable film-forming polymer dissolved in an aqueous medium.[57] The print coater introduced for Type 41 and subsequent black and white systems is a swab saturated with an acidic alcohol-water solution of a basic polymer. Swabbing the print both rinses residual reagent away from the image silver and deposits a coating which quickly dries to a tough, impermeable polymeric layer. Prints so protected are durable and stable; they have demonstrated outstanding stability under severe archival test conditions.

Polaroid coaterless 3000 films,* yielding prints which are stable without after-treatment, deposit image silver in depth well within a receiving layer of regenerated cellulose,[46] where the silver is protected from surface abrasion and atmospheric attack. The viscous pod reagent employs as developing agents substituted hydroxylamines[58] with colorless, inert oxidation products, and as silver halide solvents sulfur-free cyclic imides[59] which leave no surface residue. Additional protection may be effected by auxiliary silver image stabilizers in the receiving sheet[60] and an underlying layer of an immobile polymeric acid[46] to abstract and neutralize excess alkali.

The Type 46L and 146L transparency images, formed in the layer of viscous reagent rather than in a preformed layer, are stabilized by momentary immersion in a solution of stannous chloride, which renders residual developer inactive by neutralizing the alkali, reduces quinone and crosslinks the polymeric thickener to form a tough and durable layer.[61]

Offset Printing from One-Step Images

The recognition that transferred image silver exists as a near-continuum at high densities led to the design of a system for making offset printing masters directly from materials exposed and processed in a one-step camera. For this purpose the image silver is confined to a very thin surface layer of the receiving sheet. When printing ink is applied to the image layer, the silver image and image-free areas accept the ink differentially, and the silver image, bearing an image in terms of ink, may then be used for printing.[62] If exposures are made through a halftone screen located at the focal plane of an amateur or professional camera, offset masters and prints are readily prepared from continuous tone images.

Additive Color Processes

The SX-70 process and the other one-step color processes discussed in the section on *Dye Image Processes* are subtractive processes in which positive images are formed of the subtractive primary colors—cyan, magenta and yellow—and superimposed to produce a full color image. One-step additive color processes, which use positive images of silver to modulate the additive primaries—red, green and blue—have also been described and successfully demonstrated.

One example is a lenticular color process,[63] in which both emulsion and receiving layer are coated on a base bearing minute lenticules on its opposite surface. The film is exposed by passing light through a banded color filter and through the lenticules to form separately positioned sets of color records behind each lenticule. The film is then processed to yield a positive image in silver in the image-receiving layer, and the positive image is viewed in full color by projection through the banded color filter. An analogous lenticular system for black and white stereoscopic photography and projection uses oppositely oriented polarizers in place of the color bands.

Bases bearing additive color screens of red, green and blue line or grid elements may also be used as support for an emulsion and an adjacent image-receiving layer to form additive color transparencies.[64] The emulsion is exposed through the additive color screen and then processed to deposit a positive silver image in the receiving layer. The positive image and the additive screen are projected in registration to produce an additive color image.

In these projection systems the developed emulsion layer may be separated from the positive image-bearing layer after transfer or it may be retained[65] and the image viewed in its presence.[66] Indeed, the positive image may be formed in the emulsion layer. Systems of the latter types take advantage of the high covering power of transferred positive silver images, which is typically five to six times that of the developed negative images and in special cases as high as nine or ten times the negative covering power.

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*Types 20C, 87 and 107C.

DYE IMAGE PROCESSES

The first one-step color film, Polacolor Land Film, was introduced in 1963, following more than 15 years of experimentation, synthesis and invention. Land, Rogers and several of the other scientists who participated in the Polacolor research effort reported jointly on this work before the Society of Photographic Scientists and Engineers in May, 1963.[67] The report included a discussion of the earlier one-step color processes investigated and described the evolution of many of the unique features of the working Polacolor process.

Coupler Processes

As early as 1947 Land had described one-step processes based on the imagewise distribution of exhausted developers and exhausted color-forming couplers,[1] and the 1944 experiments described earlier had also demonstrated the feasibility of transferring positive dye images through developed or developing negatives. Intensive work toward a three-color, one-step process was begun by Land and Rogers in 1948.

Monochrome Image Transfer. The first processes investigated were exhausted coupler processes based on developing the exposed grains of a negative with a color developing agent in the presence of a color-forming coupler. The color components could be incorporated in the emulsion, in a separate layer or in the reagent. Upon development an immobile negative image in dye and silver formed in the emulsion layer; at the same time a positive image in terms of unoxidized developer and unused coupler was transferred to an adjacent layer. Here the transferred developing agent was oxidized and coupled with the transferred coupler to form a positive dye image.[68] Colorless, immobile oxidizing agents were incorporated in the receiving layer to make this a one-step process, and many successful monochromes were produced by this method.* Figure 12-80a is a reproduction of such a monochrome prepared in 1951. When one-step monochromes in cyan, magenta and yellow produced by the exhausted coupler process were superimposed in register the combined three-color subtractive positive was of excellent color quality. Three such monochromes could also be formed successively in register in a single receiving layer to comprise a full three-color print.[70]

Three-Color Prints from Striped Negative Elements. The next objective was to form the three dye images simultaneously and in a single sheet. While it was recognized that subtractive dye images were needed to provide white highlights in a positive reflection print and that the three positive dye images must be superimposed and continuous in order to produce saturated colors, these requirements for the positive image did not mean that the negative needed to form three continuous images. Land therefore proposed the use of an array of side-by-side or crossed stripe elements in the negative,[71a] with the elements of such size that the transferred images would diffuse laterally during transfer to overlie one another fully. With the stripe arrangement negative image formation could take place in each element independently and simultaneously. A suitable element width would be of the order of the diffusion distance, or approximately .004 in. (0.1 mm), corresponding to 250 elements/in. (10 elements/mm).

There were several new problems associated with constructing a set of stripes, each containing all of the components required to make a monochrome image. To make each stripe an integral single layer element would require the incorporation into the emulsions of components which might be inimical to emulsion sensitivity; the coupler and developer would tend to transfer prematurely when alkali reached the element, so that imagewise control of the dye formed and transferred would be impaired; and single-layer elements could not efficiently provide the yellow filtration required to protect the red- and green-sensitive emulsions from exposure to blue light. To avoid these problems each of the side-by-side elements was coated as a multilayer structure. The construction of these multilayer elements by a series of embossing and coating operations[71b] is illustrated in Fig. 12-81. When the first such striped three-color negatives were processed, the disparate rates of reaction of the three couplers led to serious interactions between the individual color elements. The most reactive of the couplers, the cyan-forming substituted phenols and naphthols, readily reacted with oxidized developer from the adjacent elements, leading therefore to reduced color isolation and color balance.

Preformed Coupling Dyes. To overcome the problem of disparate coupling rates, Rogers sought a single reaction which would control each of three dyes independently and at a uniform rate. He tested the use in each element of an already formed soluble dye bearing a coupler group which would effect dye precipitation by reacting with oxidized developer in regions of exposure; the dye would transfer freely in unexposed regions.[72] Each of the three dyes could thus be controlled by reaction of the same coupling group, permitting their precipitation in the negative or their transfer to the receiving layer at comparable rates. The use of preformed dyes

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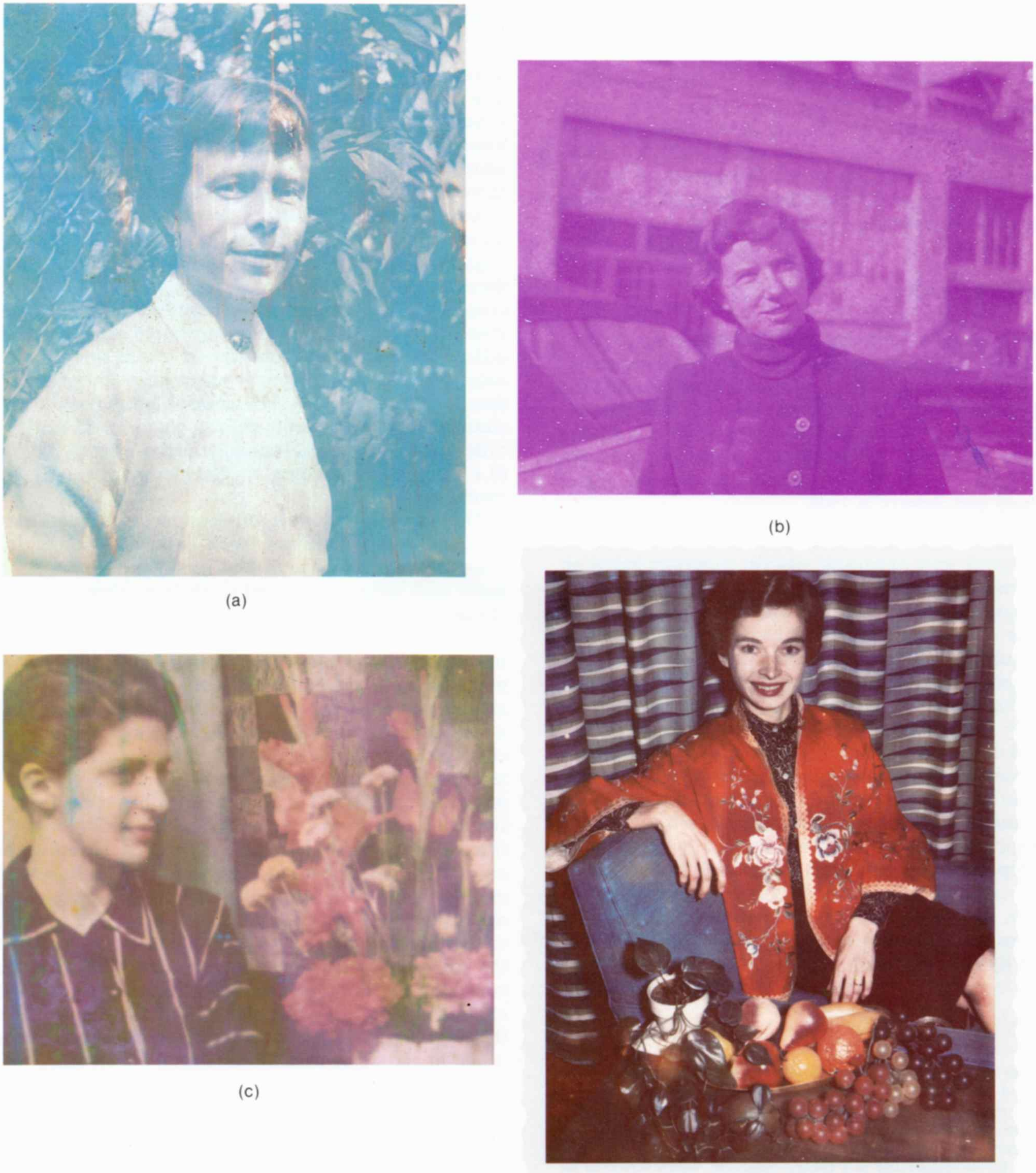
*Another useful coupler dye process transferred a positive image in terms of unoxidized color developer, using a receiving layer containing coupler and oxidizing agent. Similarly, a positive image in terms of unused coupler only could be transferred and then coupled. A positive image in terms of unoxidized developer and unused coupler could also be transferred to a fogged emulsion, which served as an oxidizing receiving layer; this procedure formed a positive dye image in a single step but left the silver halide and reduced silver to be removed in a later step.

In another coupler system, a polymeric coupler was used to provide an imagewise impermeable membrane by reaction with oxidized color developer in the regions of exposure; the negative image in impermeable polymer could then be used to control diffusion of a dye through this layer to form a positive image in an adjacent layer. Color transfer systems using developing agents containing coupling moieties have also been proposed.[69]



(a)

(b)

(c)

(d)

Fig. 12-80. (a) Monochrome made by exhausted coupler process (1951); (b) monochrome in dye controlled by negative images of bubbles (1953); (c) 3-color print using dye developer in striped negative format (1955); (d) 3-color dye developer print from continuous multilayer negative (1957).

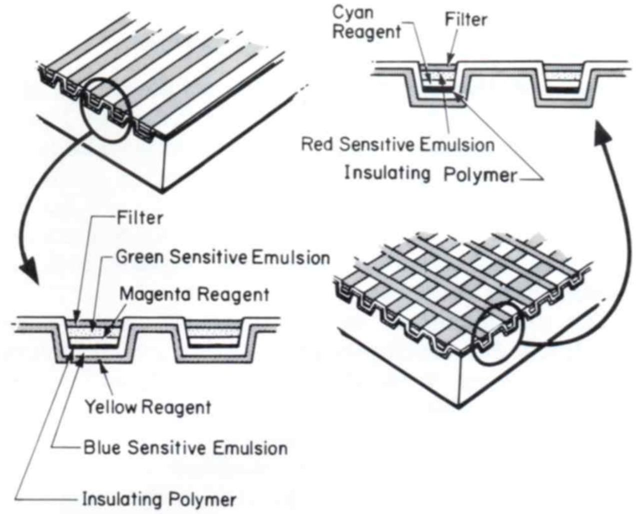


Fig. 12-81. Construction of striped color negative. First a continuous coating of the components needed to form a yellow image is prepared, and over it is coated a continuous layer of blue-sensitive emulsion. The resulting monochrome negative is embossed to form a set of grooves and the grooves are filled by successive coating and doctoring with the layers required to form the second color. The two-color assembly is again embossed to form a new set of grooves at right angles to the first set, and the components of the third monochrome unit are coated in these grooves. Each of the grooves contains in order an insulating polymer layer, a layer containing color developer and coupler, a sensitized emulsion layer and a yellow filter layer.

of this type* eliminated the disparity of reaction rates and reduced the unwanted interactions.

Dye Developer Processes

To obtain greater control of the three image-forming reactions, Rogers proposed to incorporate the developing function into preformed dyes, providing for each color component a single molecule—a *dye developer*—which could act both as a developer and as an image-forming dye.[9] Before oxidation the dye developer would be insoluble in water but soluble in aqueous alkali. Dye developer undergoing oxidation as a result of development of exposed silver halide would be immobilized, and transfer of the remaining unoxidized dye developer would produce a positive image.

Hydroquinone was recognized as a particularly useful developing group for incorporation into dye developers; its weakly acidic phenolic groups are not very solubilizing, and hydroquinones are very weak reducing agents in water. Hydroquinonyl dye developers are thus inert as developers in contact with an emulsion under neutral or acidic conditions. Aqueous alkali readily solubilizes hydroquinone, which is a strong reducing agent at high pH. Furthermore, when hydroquinone is used as the developer part of a dye developer its solubilization and oxidation reactions confer the desired solubility characteristics upon the entire molecule.

Development with Dye Developers. *Dyes with Developing Function Directly Linked.* The first dye developers synthesized were azohydroquinones, the azo group being substituted directly on the hydroquinone ring, and hydroquinone-substituted aminoanthraquinones, as shown in Fig. 12-82. These dye developers were vigorous developing agents, and they transferred to form excellent positive images. The spectra of the dyes, however, were subject to variation due to reactivity of the hydroquinone portions of the molecules, showing color shifts with oxidation of the hydroquinone and with pH change.

Insulation of Chromophore from Developer. Dye developers with insulating links to interrupt the conjugation between the developing group and the dye chromophore were synthesized to solve the problem of unwanted color shifting; and these dye developers provided excellent monochrome images with colors essentially independent of pH and state of oxidation.[78] Many insulated dye developers,[9b] including metallized dye developers,[9b,79] have been designed and synthesized to achieve desired combinations of solubility and diffusion properties, development characteristics, spectral absorption and light stability. Figure 12-83 shows the structures of dye developers with insulating links, such as were first used in Polacolor film, and Fig. 12-84 shows

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*There are additional preformed dye systems of interest for one-step processes. One class involves alkali exhaustion,[73] that is, the consumption of alkali in the regions of negative image development, which leaves unexhausted alkali free to implement transfer of a positive image in dye.

Exhausted developer processes have used reducible image dye precursors,[74] such as colorless triazolium or tetrazolium bases, reduced by unexhausted developer to their colored forms. These bases can also be used as temporary mordants for acid dyes, which are released imagewise upon reduction of the base by the unexhausted developer. Indophenols, which are colored in oxidized form, can also be reduced and solubilized by an unexhausted developer, then transferred and oxidized to form a positive dye image.

Bubbles formed upon oxidation of a developing agent such as bis-(benzene-sulfonyl) hydrazide are sufficient to prevent the transfer of a soluble dye, so that a positive image may be transferred through the unexposed regions of the developing layer.[75] Figure 12-80b is reproduced from a monochrome prepared in this way in 1953.

Dye-dropping systems[76] are based on attaching a dye to an immobile reducing agent which, upon its oxidation by an oxidized developer, will release a mobile dye. This mechanism may be used to form either negative or positive transfer images. A negative is obtained by transfer from developing areas. Development of a direct positive emulsion results in a transferred positive image. Another way of obtaining a positive is to put a dye bound to an immobile reducing agent into a layer adjacent to the emulsion, along with silver-precipitating nuclei, as are used in the silver transfer systems, and to use a reagent containing hypo; in the unexposed regions, unoxidized developer and soluble silver complex diffuse into this layer, whereupon the silver is reduced and precipitated, the developer oxidized, the dye-holding compound in turn oxidized and the dye released and transferred to a receiving layer as a positive image. Release of a dye or a dye intermediate from an immobile compound may also be effected by soluble silver ions, e.g., by the silver-assisted cleavage of a thiazolidine group.[77] An advantage to dye-dropping processes is that each of the released dyes in a three-color film is unreactive, so that there are no unwanted interactions involving the diffusing dyes.

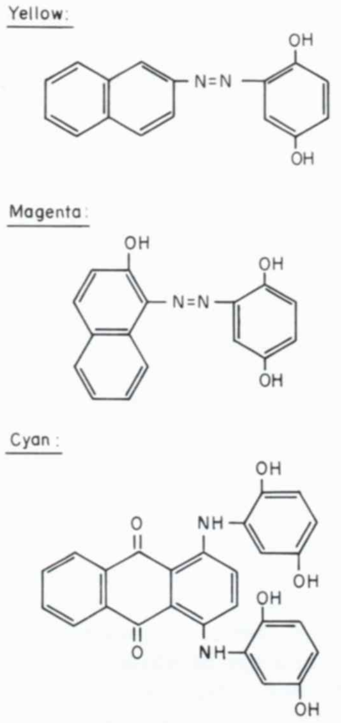


Fig. 12-82. Early dye developers.

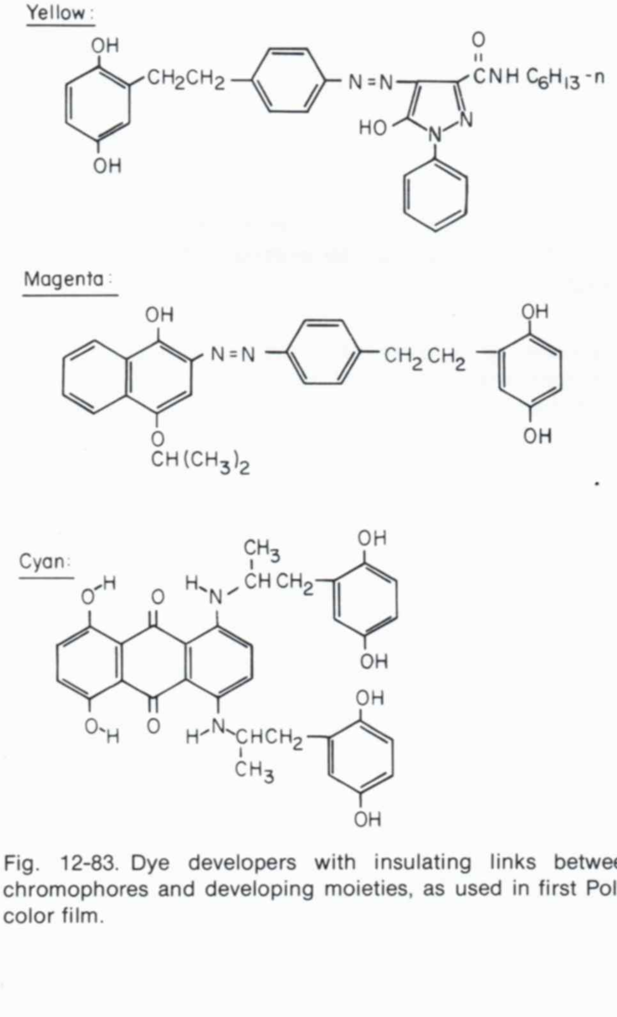


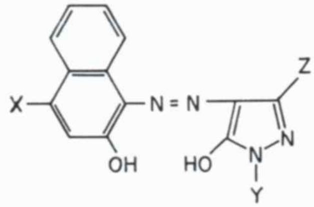
Fig. 12-83. Dye developers with insulating links between chromophores and developing moieties, as used in first Polacolor film.

insulated metallized dye developers of the types used in the SX-70 and Polacolor 2 color negatives.*

Metallized Dye Developers. The metallized dye developers used in both the SX-70 and Polacolor 2 processes yield brilliant images of outstanding stability to light.[80] The metallized cyan dye developer is based on copper phthalocyanine, a pigment well known for its stability. Addition to the molecule of solubilizing groups and developer groups converts the pigment into an alkali-soluble developer.

The chromophores of the magenta[81] and yellow metallized dye developers (Fig. 12-84) are chromium complexed dyes. While chromium is capable of forming complexes with either one or two azo dye molecules per chromium atom, the 1:1 complexes exhibit superior spectral purity. A colorless, modified acetylacetone ligand is introduced to occupy two of the remaining coordination sites of the chromium atom, in order to minimize reactions with gelatin that might hamper diffusion of the dye through gelatin-containing layers of the negative. The colorless ligand also serves as a convenient site for attachment of the developer moiety.

A general structure for the class of naphtholazopyrazolone dyes from which the magenta dye developer was derived is:



X, Y and Z in this general structure are substituents which may be varied to influence the spectral absorption of the magenta chromophore. The color is also influenced, but to a lesser extent, by the choice of colorless ligand. The yellow dye developer is similarly derived from the 1:1 chromium complex of an *o, o'*-dihydroxyazomethine dye, using the same modified acetylacetone ligand.

Auxiliary Developers. The efficiency of development and image formation with dye developers may be increased by the addition of small auxiliary or "messenger" developer molecules of greater alkali solubility and higher diffusion rate than the dye developers. Because of its superior mobility an auxiliary developer can more quickly reach the exposed grains to initiate development, and its oxidation product can in turn oxidize and immobilize the slower moving dye developer.[9a] (See Figs. 12-5 and 12-7, included with earlier discussion of

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*The Polacolor film introduced commercially in 1963 will be referred to hereafter in this chapter as Polacolor 1, for convenience in distinguishing it from Polacolor 2, introduced in 1975. The use of metallized dye developers in the SX-70 process dates from its introduction in 1972.

SX-70 system.) Phenidone (1-phenyl-3-pyrazolidone) and Metol (N-methyl-*p*-aminophenol sulfate) were among the first auxiliary developers used; later systems included highly active substituted hydroquinones,[82] both alone and in combination with Phenidone.[83]

Negatives Incorporating Dye Developers. *Three-Color Striped Dye Developer Negative.* When early dye developers were substituted for couplers and color developers in the striped three-color negative configuration, color balance and isolation were vastly improved. Figure 12-80c is a reproduction of a color print from a striped dye developer negative made in 1955. Prints of this type, although promising in color isolation, were subject to some inherent limitations. Colors were not highly saturated, being somewhat handicapped by the restriction of each dye to one-third of the area of the negative, and there was still some interaction between the elements at their common edges.

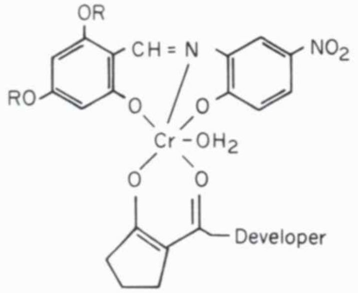
Hold-Release Processing with Dye Developers; Continuous Layers. Images from continuous monochrome dye developer negatives offered considerable advantage in color saturation over images from striped units of restricted area. Rogers and Land recognized that it would be feasible to use a stack of three such monochrome negatives coated sequentially if unwanted interactions could be avoided. They conceived holding each dye developer in the vicinity of its assigned emulsion until substantial development had taken place and then allowing it to transfer.[84] This type of hold-release action was facilitated by the selection of dye developers capable of developing rapidly and diffusing relatively slowly, as illustrated in Fig. 12-85, which shows characteristic rates of development and positive image formation of a monochrome using a Polacolor 1 magenta dye developer.

When an integral, three-color, "stacked" negative formed of three continuous monochrome units was processed, the sequential penetration of alkali through the layers assisted in color discrimination by providing stepwise initiation of development in the three monochromes. Furthermore, diffusion of the dye developers through the layers was much slower than the diffusion of alkali, and this rate difference facilitated the initiation of development in each of the monochrome units before the start of dye transfer.

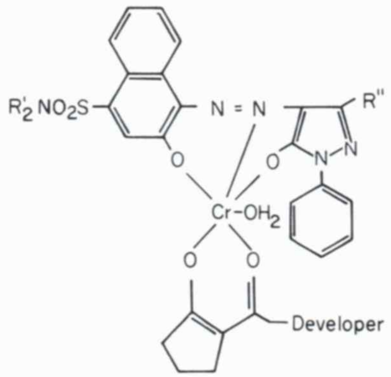
Barrier Interlayers. Unwanted interactions between the dye developers of one monochrome unit and the exposed grains of another were further reduced by the auxiliary developers and by the intercalation of temporary barrier coats which introduced time delays.[84] Useful barrier layer mechanisms for providing appropriate delays included the controlled rate of hydrolysis or rate of solution of the barrier material and the degree of spatial separation. Among suitable barrier materials were cellulose esters and permeable polymers such as polyvinyl alcohol and gelatin.

Figure 12-80d reproduces a 1957 print transferred from a negative in which barrier interlayers comprising

Yellow:



Magenta:



Cyan:

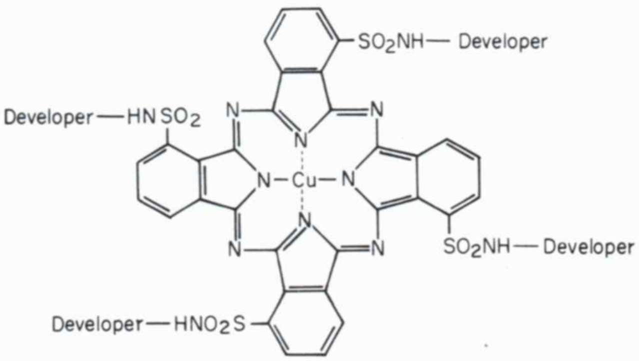


Fig. 12-84. Metallized dye developers of types used in the SX-70 and Polacolor 2 processes.

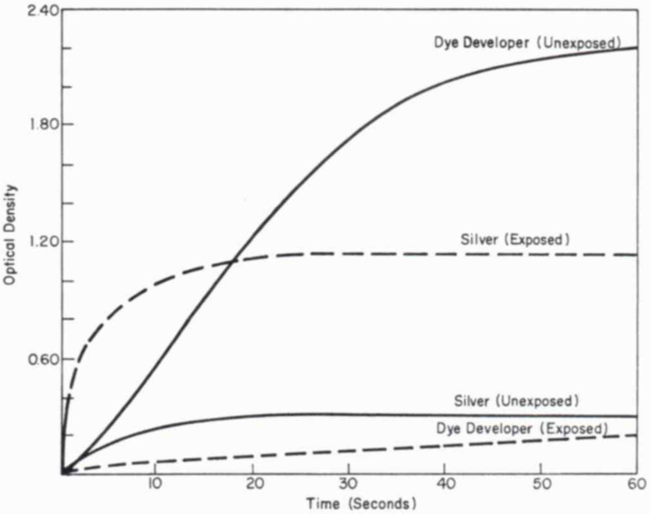


Fig. 12-85. Rates of development and of dye image formation in a Polacolor 1 magenta monochrome, in regions of no exposure and full exposure.

cellulose acetate hydrogen phthalate and cellulose acetate were used to provide hold-release action during processing. Pictures made from negatives of this type were characterized by high color saturation and good isolation and balance. Gelatin interlayers,[84,85] which operated primarily by spatial separation, were utilized in the Polacolor 1 negative to avoid the large-scale use of organic solvents in the negative coating facilities which were then available. In SX-70 and Polacolor 2 negatives, water-based barrier layers comprising combinations of latices and water-soluble polymers are used.[86]

The Polacolor Process. *Polacolor Negative.* Polacolor negative structures are shown in cross-section in Figs. 12-86 and 12-87. In these negatives, as in the SX-70 negative described earlier, each of the dye developers is initially positioned in a layer just behind the silver halide emulsion layer of complementary spectral sensitivity by which it will be controlled during processing. The dye developer may be coated as an oil dispersion[9a] or as a solid dispersion[87] in an alkali-permeable polymer—e.g., gelatin. The three monochrome units, in the order encountered during exposure, comprise a blue-sensitive emulsion overlying a yellow dye developer layer, a green-sensitive emulsion over a magenta dye developer and a red-sensitive emulsion over a cyan dye developer.

Formation and Distribution of Polacolor Images. During Polacolor processing the viscous alkaline pod reagent forms a thin layer which temporarily laminates the negative and the positive receiving sheet together. The liquid of the reagent is rapidly absorbed and the sheets are correspondingly swelled, reducing the reagent layer to a small fraction of its original thickness and bringing the surfaces of negative and positive sheets into close contact. As the negative swells, each of the solubilized dye developers moves into its associated silver halide emulsion and the auxiliary developer permeates all the layers of the negative. Where the emulsion has been exposed, the silver halide is reduced and the dye developer oxidized and immobilized. In unexposed areas, the dye developer remains soluble and passes through the emulsion toward the positive image-receiving layer, where it is made fast. Figure 12-87b shows a Polacolor 2 negative in cross section after partial swelling by aqueous alkali, and Fig. 12-87c shows a section of a Polacolor 2 positive image at the same magnification.

Color Isolation and Balance. The control of relative rates of development and transfer is critical for color isolation and balance; as mentioned earlier, the exposed grains of each emulsion must be substantially developed before a dye developer assigned to a different emulsion reaches them, and both barrier coats and auxiliary developers assist in effecting appropriate hold-release action. Additional steps are taken to prevent the undeveloped grains in each emulsion layer, whether exposed or not, from undergoing development after the dye developers have begun to move through the layers. Deactivation of the emulsions after a predetermined time period may be accomplished by the release of a low solubility silver ligand, such as a mercaptan.[88]

Still another hazard to color isolation in the multilayer structure is the possibility of reaction of dye developers with one another. Even if development is completed independently in each emulsion before unoxidized dye developer from another monochrome unit reaches it, the arriving unoxidized dye developer may reduce and release the already oxidized dye developer and thus exchange with it. The use of quaternary compounds, which may react with oxidized developer to form a less mobile species, assists in minimizing interactions of this type.[89,90]

The Image-receiving System; Stabilization. Image-receiving layers for the earliest dye developer systems included polyamides, polyvinyl alcohol and gelatin. Particularly useful receiving layers were water-swellable polymers containing mordants for the dye developers.[9a,91] Following transfer of the dye developer images to the image-receiving layer further steps were needed to stabilize the print. Swabbing its surface with a print coater wet with dilute acid after separation from the negative was the first stabilization procedure used.[92] Initial production of Polacolor roll film (Type 48) included such a print coater.

Shortly before the commercial introduction of Polacolor 1, major innovations provided a self-washing receiving sheet[93] which eliminated the need for the print coater and at the same time produced prints of increased luminosity and improved stability to light. The receiving sheet which performs these functions has three active layers, shown in schematic form in Fig. 12-88. Closest to the surface is the polymeric receiving layer containing a mordant for the image dyes. Below the mordant layer is a layer of a timing polymer,[93,94] which determines the

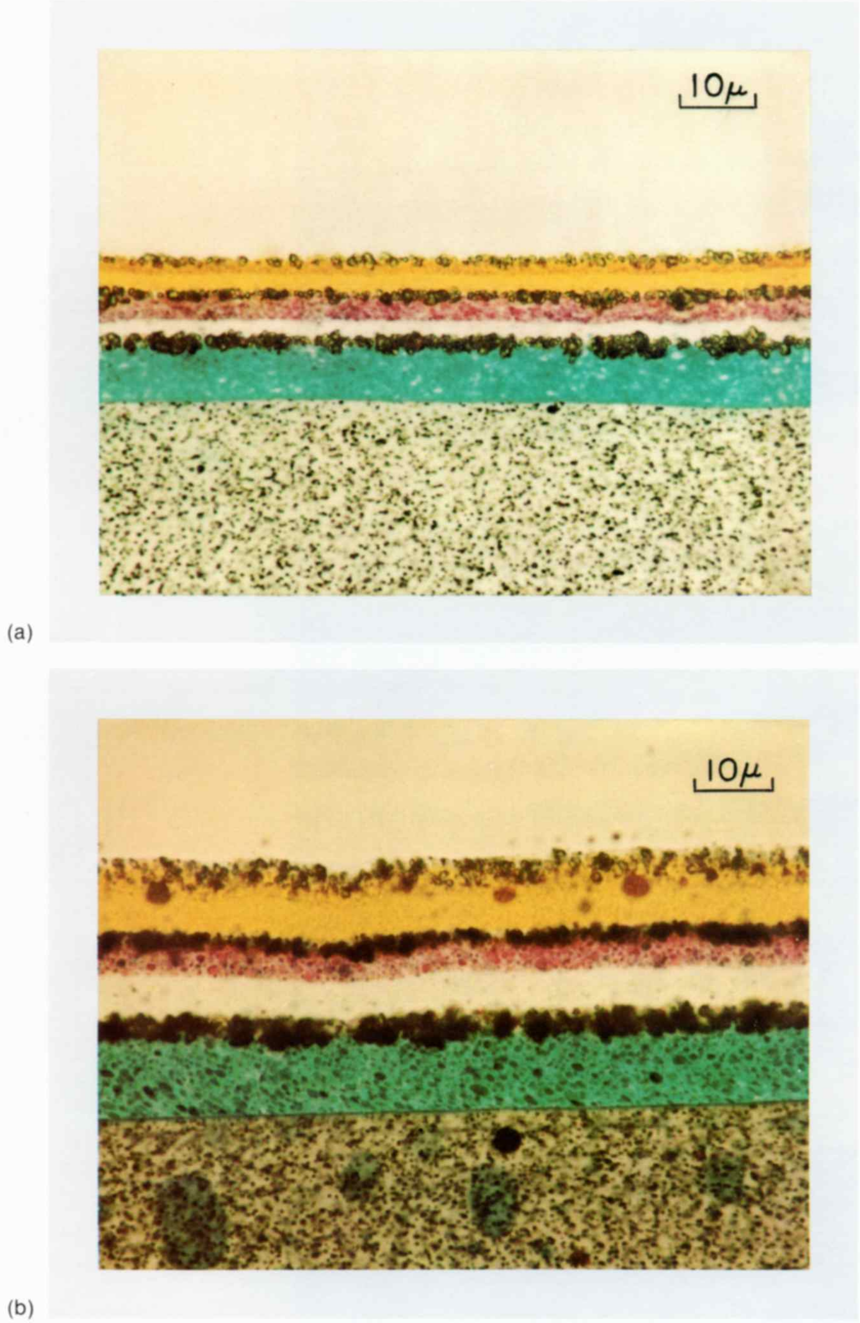


Fig. 12-86. Cross sections of Polacolor 1 negative. The upper interlayer contains an auxiliary yellow filter dye. (a) Unprocessed negative; (b) negative after partial swelling with aqueous alkali.

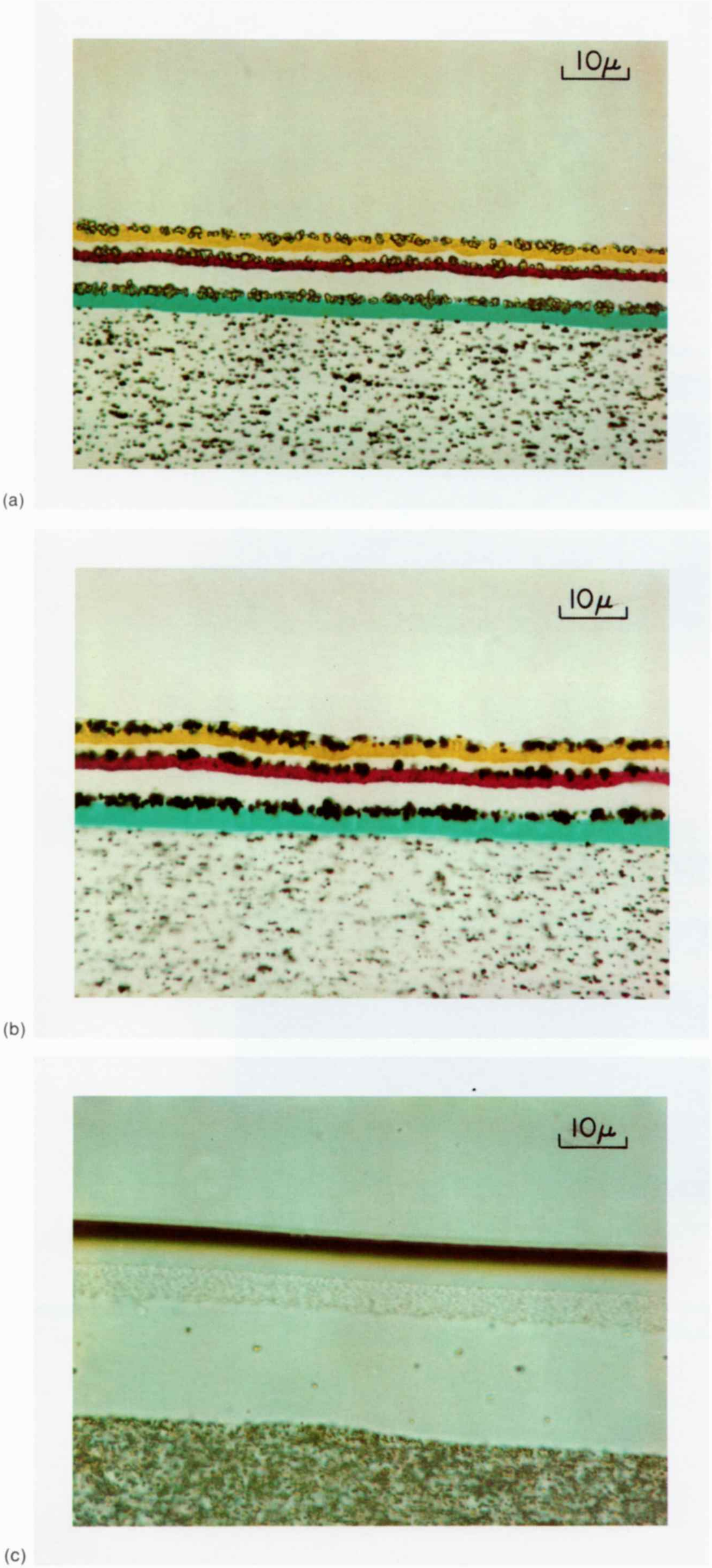


Fig. 12-87. Cross-sections of Polacolor 2 negative and positive sheets. Section (a) is from an unprocessed negative; (b) shows a negative partially swelled with aqueous alkali; and (c) is a section of a positive image of maximum density. Note that this negative is considerably more compact than the Polacolor 1 negative shown in Fig. 86.

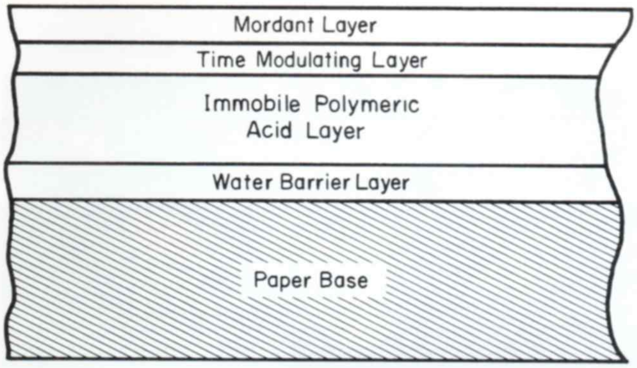


Fig. 12-88. Schematic cross section of Polacolor receiving sheet.

length of time the process will remain alkaline. Below the timing layer is a layer of an immobile polymeric acid. The immobile polymeric acid captures alkali ions and retains them, so that a buffering salt is not returned to the system as it would be with a nonpolymeric acid. The net result is that water is returned in place of alkali. The dye developers are rendered immobile and inactive as the result of the reduction of pH, and the irreversible entrapment of the alkali ions deep within the structure prevents the salting out of residues on the print surface upon separation from the negative.

The Processing Step. Figure 12-89 demonstrates the rapid rates of development of the three silver images in a Polacolor 1 negative and the less rapid rates of deposition of the three positive dye images. As image deposition in the mordant layer of the receiving sheet nears completion, the timing layer permits the polymeric acid layer to begin alkali extraction, as described above, which continues over several minutes. Figure 12-90 shows the rate of pH reduction in a Polacolor 1 positive print after separation from its negative.

Despite the requirements of concomitant developing, dissolving, transferring, mordanting and stabilizing components of three independent monochrome images which initially overlie one another, Polacolor processing is operationally simple. The negative and positive sheets are peeled apart after 60 sec imbibition and the negative discarded. The full color print is ready for immediate viewing with no further manipulation; its surface quickly dries to a hard gloss, and the finished print is durable and stable.

The Polacolor one-step process remains a significant departure from conventional color processing technology. The wet processing of conventional color films and prints involves lengthy multistep darkroom procedures, critical in both time and temperature and inherently limited to the professional finisher or the advanced amateur with a well-equipped darkroom.

The Polacolor process has made it possible for the photographer to obtain a full color print of high quality under ambient conditions, and to obtain it rapidly enough to permit simultaneous observation of print and subject. These capabilities have provided important new opportunities for creative color photography by both amateur and professional and for scientific color photography in many fields. In April, 1976, the making of 8 × 10 in. and 20 × 24 in. Polacolor 2 photographs was demonstrated, and replicas of museum paintings as large as 3 × 6 ft photographed at actual size, using Polacolor 2 film and process in a full size camera (40 × 80 in. image

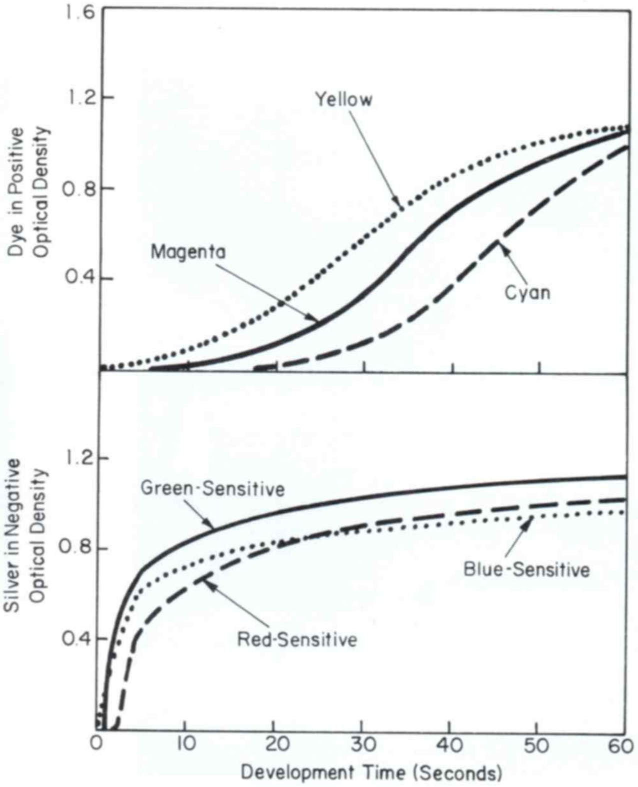


Fig. 12-89. Relative rates of image formation in the Polacolor 1 process. Upper curves show dye deposition in the positive image-receiving layer for regions of no exposure. The lower curves show development of silver in the negative in regions of full exposure.

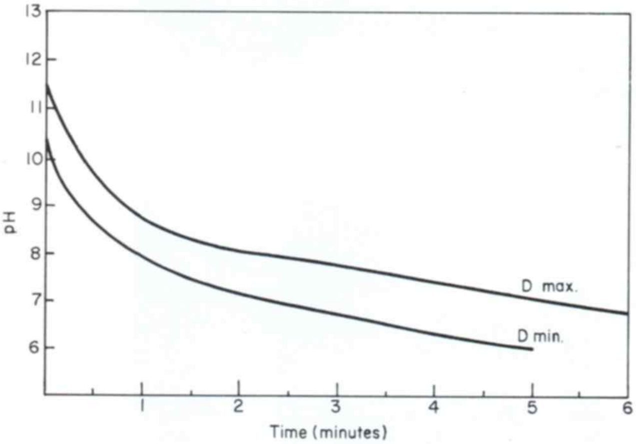


Fig. 12-90. pH drop of a Polacolor 1 positive print after separation from its negative. The pH at the time of separation will have dropped from 14 to between 11 and 12, a pH low enough to inhibit many undesirable oxidation phenomena.

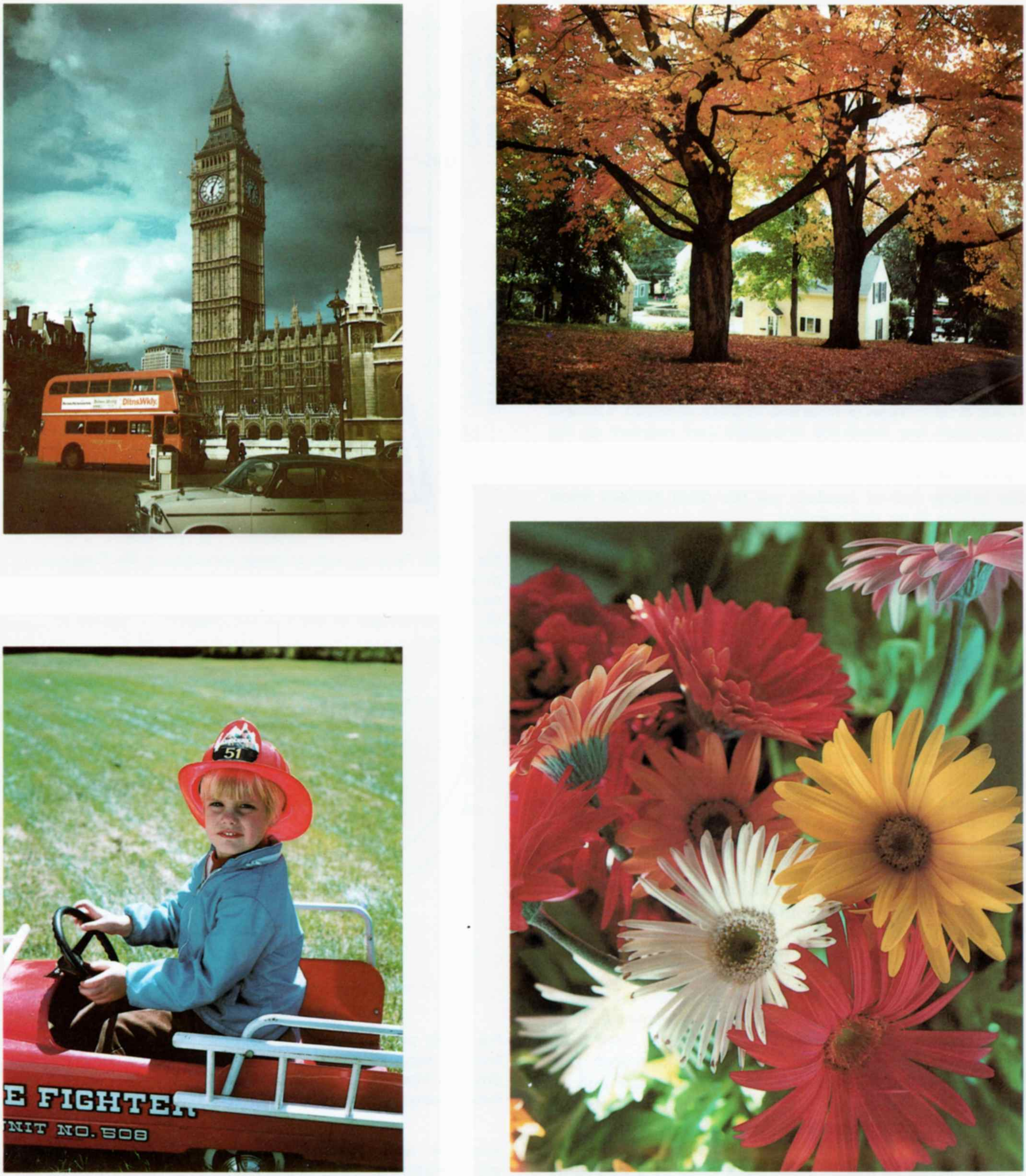


Fig. 12-91. Reproductions of Polacolor photographs. See also Figs. 12-10, 27, 86 and 87.

area), were exhibited.[95] Figures 12-27 and 91 are examples of Polacolor photographs, as are the optical micrographs shown in Figs. 12-10, 86 and 87.

Some Major Differences Between Polacolor and SX-70. Both the SX-70 color process described in an earlier section of this chapter and the Polacolor process utilize dye developers, but the two films differ in major respects.

The requirement that the SX-70 film unit be in its final format from start to finish means that all of the reactive materials must be present within the unit from the time of manufacture. The entire structure must, of course, be stable over a wide range of ambient temperatures. Furthermore, after exposure of the negative the complex set of reactions which are involved in forming the negative and positive images and stabilizing the system must be well coordinated over a wide temperature range. Following completion of these reactions, all of the reaction products must coexist in a new stable structure.

Whereas in the Polacolor system the positive image-forming reactions are terminated by stripping away the negative, thereby preventing continued transfer of solubilized dye developer, the SX-70 integral structure requires that these reactions, as well as others, be brought to completion at the appropriate stage without removing or discarding anything at all. Stabilization of an SX-70 film unit thus involves all of the layers of the negative as well as the positive. In addition to providing a stable environment for the positive image dyes, as in Polacolor, the reactions which take place during pH reduction must render immobile the dye developer which is left in the negative, so that unwanted further transfer cannot take place, and render inert all other reactants and reaction products. Many of the stabilizing reactions, which are not discernible to the observer, take place within the film unit concomitantly with the conversion of the opacifying indicator dyes from colored to colorless state. All of these reactions accompany the visible materialization of the final, full-color positive image.

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